"THE KINETICS OF SOME REACTIONS IN SOLUTION INVOLVING THE FERRICYANIDE ION."

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for the degree of Doctor of Philosophy,

by

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PREFACE.

The work described in this thesis was carried out in the laboratories of the Chemistry department of Bedford College, University of London, under the supervision of Dr. J.W.Smith.

The author is very grateful to Professor E.E.Turner for providing facilities for the investigation and to the Council of Bedford College and the Governors of Colston's Girls' School, Bristol, for the award of scholarships without which the work would have been impossible. Finally, she would like to express her most sincere thanks to Dr. J.W.Smith for his kindly encouragement and helpful supervision.

CONTENTS.

ABSTRACT.

The reaction between potassium iodide and potassium ferricyanide has been studied by several workers, using the Harcourt - Esson method to follow its progress but the results obtained have not furnished unambiguous evidence regarding its mechanism. Some preliminary measurements confirmed the previous experimental evidence but suggested that a side reaction between the ferricyanide and thiosulphate ions may be a possible cause of the complications arising. A study of the latter reaction has therefore been a major subject of the present work.

The reaction has been followed by titration of the sodium thiosulphate remaining after various time intervals with a standard solution of iodine, using starch as indicator. The rate curve for this change in unbuffered solutions shows an initial period of rapid reaction, followed by a period of retardation and a further one of slight acceleration before the normal steady decrease in rate with time takes place. These stages are accompanied by marked changes in the pH of the solution. Some, but not all of these features are removed in buffered solutions.

The reaction is apparently of first order in acid solutions and of second order under neutral or alkaline conditions. It is accelerated by the presence of tetrathionate ions and retarded by ferrocyanide ions and it shows a

pronounced positive neutral salt effect. A mechanism for the reaction is suggested on the basis of these observations which accounts satisfactorily for the behaviour in neutral and alkaline solutions.

INTRODUCTION.

The original object of the present work was to clarify the rather inconclusive position which exists with regard to the kinetics of the reaction between ferricyanide and iodide ions.

When solutions of potassium ferricyanide and potassium iodide are mixed an equilibrium is set up thus

$$2\ Fe(CN)_6^{'''} + 2\ I^{'} \rightleftharpoons 2\ Fe(CN)_6^{''''} + I_2$$

Unlike most reactions between ions of <u>like</u> charge this equilibrium state is attained relatively slowly. The simplest manner of formulating the forward reaction would be

$$Fe(CN)_6^{'''} + I^{'} = Fe(CN)_6^{''''} + I$$

followed by a rapid step

$$2\ I = I_2$$

It would therefore be expected to follow second order kinetics i.e. of first order with respect to each reactant. A difficulty arises in regard to its study, however, on account of the disturbing effect of the reverse reaction. In the first systematic study of the reaction, therefore, Donnan and Le Rossignol[1] adopted the procedure originally devised by Harcourt and Esson[2]. This comprised adding successive quantities of sodium thiosulphate to their

reaction mixture and observing the time which elapsed before the liberation of free iodine, as indicated by starch.

This procedure has two advantages, (a) the free iodine is removed as rapidly as it is formed and hence the back reaction is completely stopped, (b) the iodide ion concentration is maintained almost constant throughout the reaction thereby facilitating the interpretation of the results.

The latter circumstance presupposes that the solution is not appreciably diluted by the successive additions of sodium thiosulphate solution: to ensure this Donnan and Le Rossignol used a very concentrated solution of sodium thiosulphate. By this technique they measured the rates of the reaction with various initial concentrations of potassium ferricyanide (N/80 - N/20) and constant concentration of potassium iodide (N/2). On calculating the rate constants from the results for each kinetic experiment, the values obtained for $k_1 = 1/t \log a/a-x$ decreased progressively with increasing time, but those for $k_2 = 1/t\ (1/a-x - 1/a)$ remained roughly constant with time, so they inferred that the reaction was of second order with respect to ferricyanide ions. A puzzling feature, however, was that the second order rate constant k_2 appeared to decrease with increasing initial concentration of ferricyanide. They inferred from this that the rate constant is a function

also of the total ferricyanide plus ferrocyanide concentration. This conclusion appeared to be confirmed by the observation that the rate constant for an initial mixture which was N/40 in both ferricyanide and ferrocyanide yielded the same rate constant as one which was initially N/20 in ferricyanide and contained no ferrocyanide. As this represents a "half reacted" state such a result is not surprising.

Under these circumstances they inferred that it was not justifiable to apply any method for determining the order which was based on varying dilution, since these assume the velocity constant to be intrinsically independant of concentration. They therefore rejected the use of the Noyes - van't Hoff formula

$$\underline{m} = 1 + \frac{\log t_1/t_2}{\log c_2/c_1}$$

and inferred that $\underline{m}$, the order of the reaction with respect to ferricyanide ions, is two.

On the other hand when studying the effect of varying the iodide concentration, whilst maintaining the initial ferricyanide concentration constant, they applied the Noyes - van't Hoff relationship and so found that $\underline{n}$, the order of reaction with respect to iodide ions appeared to be three, suggesting that the primary reaction was of the form

$$2\ Fe(CN)_6^{'''} + 3I^{'} = 2\ Fe(CN)_6^{''''} + I_3^{'}$$

The apparent dependence of the rate constant on the sum of the ferricyanide and ferrocyanide concentrations they suggested might arise through slight dissociation of the ferricyanide ions into ferric ions and cyanide ions, the former being the entity which actually reacts with the iodide ion. On the assumption that the ferricyanide and ferrocyanide ions have approximately equal instability constants, they showed that such a view would account for the slight minimum in the values of k_2 when calculated from each successive measurement as well as for the fact that the mean value of k_2 was inversely proportional to $\underline{a}^{0.8}$ where $\underline{a}$ was the initial concentration of ferricyanide.

Such a hypothesis, however still leads to the inference that the rate determining step in the reaction has the form

$$2\ Fe^{+++} + 3\ I^{'} = 2\ Fe^{++} + I_3^{'}$$

A subsequent reexamination of this reaction by Just[3] confirmed the experimental results of Donnan and Le Rossignol but he interpreted them differently. Applying the Noyes - van't Hoff formula he concluded that the reaction is of the first order with respect to ferricyanide and of the second order with respect to iodide, giving an overall third order reaction.

Other noteworthy observations made by Just include (a) that the velocity is very markedly increased by the

addition of indifferent potassium salts. This was interpreted by him as indicating that it is undissociated potassium ferricyanide which is the real reactant, but would now be regarded as the ordinary salt effect to be expected for a reaction involving ions with charges of like sign.

(b) the reaction is retarded by ferrocyanide but not by iodine.

(c) the reaction is accelerated by both cyanide and fluoride ions and also by hydrogen ions.

(d) the reaction is retarded by hydroxyl ions.

Similar conclusions to those of Just regarding the order of the reaction were also drawn by von Kiss[4] who also emphasised the accelerating action of hydrogen ions.

These earlier observations and the arguments used in interpreting them have been discussed at some length as they have considerable bearing on the investigations made in this work and on their interpretation. It is evident that there are a number of points which are by no means fully explained by any one of the suggestions which have been made. These include

(a) the retarding action of ferrocyanide

(b) the fact that the disappearance of ferricyanide during any individual experiment at constant iodide concentration follows more nearly a second order than a first order law, although the rate constants as calculated from individual

readings invariably pass through a minimum. This is obviously interconnected with the retardation by ferrocyanide ion.

(c) the acceleration by hydrogen ion.

The initial object of this investigation was to study these points with a view not only to their interpretation but to find the reason why the reaction should be of second order with respect to iodide ion. Hence the preliminary experiments involved a repetition of previous studies upon the ferricyanide - iodide system.

Solutions of potassium ferricyanide, potassium iodide and starch were mixed and brought to constant temperature in a thermostat at 25^{0}. Small known volumes of a concentrated solution of sodium thiosulphate were added and the time elapsing before a blue colour was developed was noted. Further additions of thiosulphate were then made to obtain a series of results. Providing that the sodium thiosulphate solution is concentrated, it is reasonable to assume that the concentration of iodide ions will be constant. Hence by using different initial strengths of potassium ferricyanide it is possible to calculate the order of reaction with respect to this substance. The results are given in Table A. They are in very satisfactory agreement with the values obtained from Donnan and Le Rossignol's figures, the average for which was about 0.8.

Table 1.

Original concentration of $K_3Fe(CN)_6$. (c)	% reaction.	Time (secs.) (t)	Order of reaction. $n = 1 - \frac{\log t_1/t_2}{\log c_2/c_1}$
0.0277N	10.90	2496	0.84
0.0138N		2760	
0.0277N	21.80	5494	0.81
0.0138N		6259	

However, amongst the factors which may affect the rate of this reaction is the presence of thiosulphate ions and of the oxidation product, tetrathionate ions. In the reaction as carried out by the previous workers the thiosulphate ion concentration was relatively low at all times and consequently, although the question of the direct reaction between ferricyanide and thiosulphate ions was considered, both by Just and von Kiss, they concluded that under their experimental conditions this reaction would be of negligible significance. Possible effects arising from the presence of tetrathionate ions do not appear to have been taken into consideration. It was therefore considered to be desirable to investigate the effect which the presence of thiosulphate would have by making separate measurements of the rate of the

ferricyanide - thiosulphate reaction. This proved to have so much interest on its own account that its study forms the main part of the work described in this thesis. The results obtained, however, give an indication of factors which may affect the course of the ferricyanide - iodide reaction. Some studies had already been made of this reaction by Sandved and Holte[5] but their published paper was not available when the work was begun and when it did become available it was found that only certain aspects of the reaction had been studied.

CHAPTER 1.

PRELIMINARY EXPERIMENTS ON THE REACTION BETWEEN FERRICYANIDE AND THIOSULPHATE IONS.

Section 1.

(1) Establishment of a method for following the course of the reaction.

A series of experiments was carried out with mixtures of standard solutions of sodium thiosulphate and potassium ferricyanide to ascertain the most suitable conditions for studying the reaction occurring between these two substances.

Firstly equal volumes of 0.1N solutions of these compounds were mixed and allowed to stand at room temperature. After certain intervals of time samples were withdrawn and run into an excess of standard iodine solution, thus enabling the unused sodium thiosulphate in the mixture to be determined by back titration.(6) These results were inconsistent. (See Table 1.(1))

Table 1.(1)

Reaction followed by back titration of unused sodium thiosulphate, at room temperature.

Time in mins.	% reaction.
0	0.0
128	5.7
235	1.7
473	7.0

Next these experiments were repeated but this time the samples of mixture withdrawn were run into iodine cooled with ice; again the results were inconclusive. This method however, indicated that a greater percentage of reaction had occurred in a given time than was apparent by the first method. A typical series of results is shown in Table 2(1).

Table 2(1).

Reaction followed by back titration of unused sodium thiosulphate at 0°C.

Time in mins.	% reaction.
0	0.0
148	19.5
261	20.8
425	17.8
1451	34.4

It seems likely that the following reactions were taking place:-

$$2\,Fe(CN)_6^{'''} + 2\,S_2O_3^{''} \rightleftharpoons 2\,Fe(CN)_6^{''''} + S_4O_6^{''} \qquad (1)$$

$$2\,Fe(CN)_6^{'''} + 2\,I^{'} \rightleftharpoons 2\,Fe(CN)_6^{''''} + I_2 \qquad (2)$$

Therefore it was decided to follow the reaction by direct titration of the sodium thiosulphate with iodine solution thus decreasing the error due to the occurrence of reaction (2).

Several runs were carried out in which 200c.c. mixtures

of varying concentrations of the reacting solutions were prepared and left at 25°C; 20c.c. samples were removed at intervals, run on to ice, thus freezing process (1), and immediately titrated with iodine solution using starch as indicator. The results so obtained were consistent and so this method of sampling was adopted for future use. A typical example of the results obtained by this method is shown in Table 3.(1)

Table 3.(1)

Reaction followed by direct titration of unused sodium thiosulphate at 0°C.

The mixture used contained {100c.c. 0.1N $K_3Fe(CN)_6$ / 100c.c. 0.1N $Na_2S_2O_3$} Total vol. 200 c.c.

Time in mins.	ccs. 0.1N $Na_2S_2O_3$ remaining in 20c.c. sample.	% reaction.
0	10.00	0.0
19	9.19	8.1
54	8.90	11.0
121	8.42	15.8
240	7.23	27.7
367	5.70	43.0
484	4.67	53.3

(2) General technique adopted.

After this all the kinetic experiments were carried out in a thermostat controlled to $\pm 0.02^{\circ}C$. Sodium thiosulphate solution together with all other solutions being used in a given run, apart from the potassium ferricyanide, were measured into a 250c.c. reagent bottle by means of calibrated pipettes. The stoppered bottle was then placed in the thermostat and allowed to reach thermal equilibrium, after which the required volume of potassium ferricyanide solution, also thermally equilibrated, was added from a pipette. Zero time for the reaction was taken when approximately half this solution had been added. The mixture was then well shaken. The total volume of the solution used was usually about 180c.c. thus permitting seven 25c.c. samples to be taken during the course of the reaction. These were withdrawn by a pipette after convenient time intervals and run on to ice contained in a conical flask. The residual sodium thiosulphate was then titrated in the normal manner with approximately 0.1N standard iodine solution using starch as indicator.

All reagents used in these experiments were of 'Analar' grade. The iodine solutions were prepared by dissolving resublimed iodine in pure potassium iodide solution and diluting as required.[7] The normality of this solution

was determined immediately prior to each kinetic run by titration with the sodium thiosulphate solution being used in any given experiment.

(3) The effect of the surface on the rate of reaction.

As many ions are readily adsorbed on a glass surface the possibility of complications arising from the occurrence of a surface reaction could not be excluded, so it was considered to be advisable to test at an early stage whether this reaction was in fact affected by the surface of the glass reaction vessel. For this purpose a reagent bottle was packed with short lengths of glass tubing so as to increase the area of glass surface exposed to the solution to several times that present in the bottle itself. Comparative experiments made with the packed and unpacked reaction vessels however, gave results in good agreement with one another (See Table 4.[1]) so that this source of complications could be discounted.

Table 4.[1]

Comparison of the reaction rate in packed and unpacked vessels.

a = b = 0.05M. Temperature 25.0°C.

Time in mins.	% reaction in packed vessel.	% reaction in unpacked vessel.
0	0.0	0.0
19	8.1	
38		9.6
54	11.0	
75		12.1
121	15.8	
188		22.3
240	27.7	
304		36.5
367	43.0	

In this and future tables

a = Concentration of sodium thiosulphate,

b = Concentration of potassium ferricyanide,

in the mixture.

(4) The effect of exposure to light.

The possibility of a photochemical reaction as well as a purely thermal one was studied by carrying out two parallel experiments. In the first the reaction vessel was exposed to the normal laboratory illumination, whilst in the second it was shielded by covering with tin foil. The difference in reaction rate was very small indeed so in the majority of the subsequent experiments, which were of a comparative type, such photochemical effects were neglected. In certain series of experiments however, light was rigidly excluded.(See Chapter 1. Section 2.12.)

Section 2.

Factors affecting the reaction.

The conditions for obtaining reproducible results had now been established. A typical series of results recorded when the ferricyanide and thiosulphate ions were at equal initial concentrations is shown in Table 5[1] and the general pattern of the reaction curve, as shown by plotting the percentage of thiosulphate remaining in a given reaction mixture, against time, is shown in fig. 1.

Table 5.[1]

Reaction in unbuffered solution.

a = b = 0.0425M Temperature 30.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	2hrs.	13mins.	82.76
0	4	97.83	2	58	76.40
0	9	95.65	3	56	69.77
0	15	95.29	4	55	61.77
0	28	92.93	5	58	52.96
0	43	91.66	6	58	46.87
1	3	89.93	7	31	44.24
1	43	85.48			

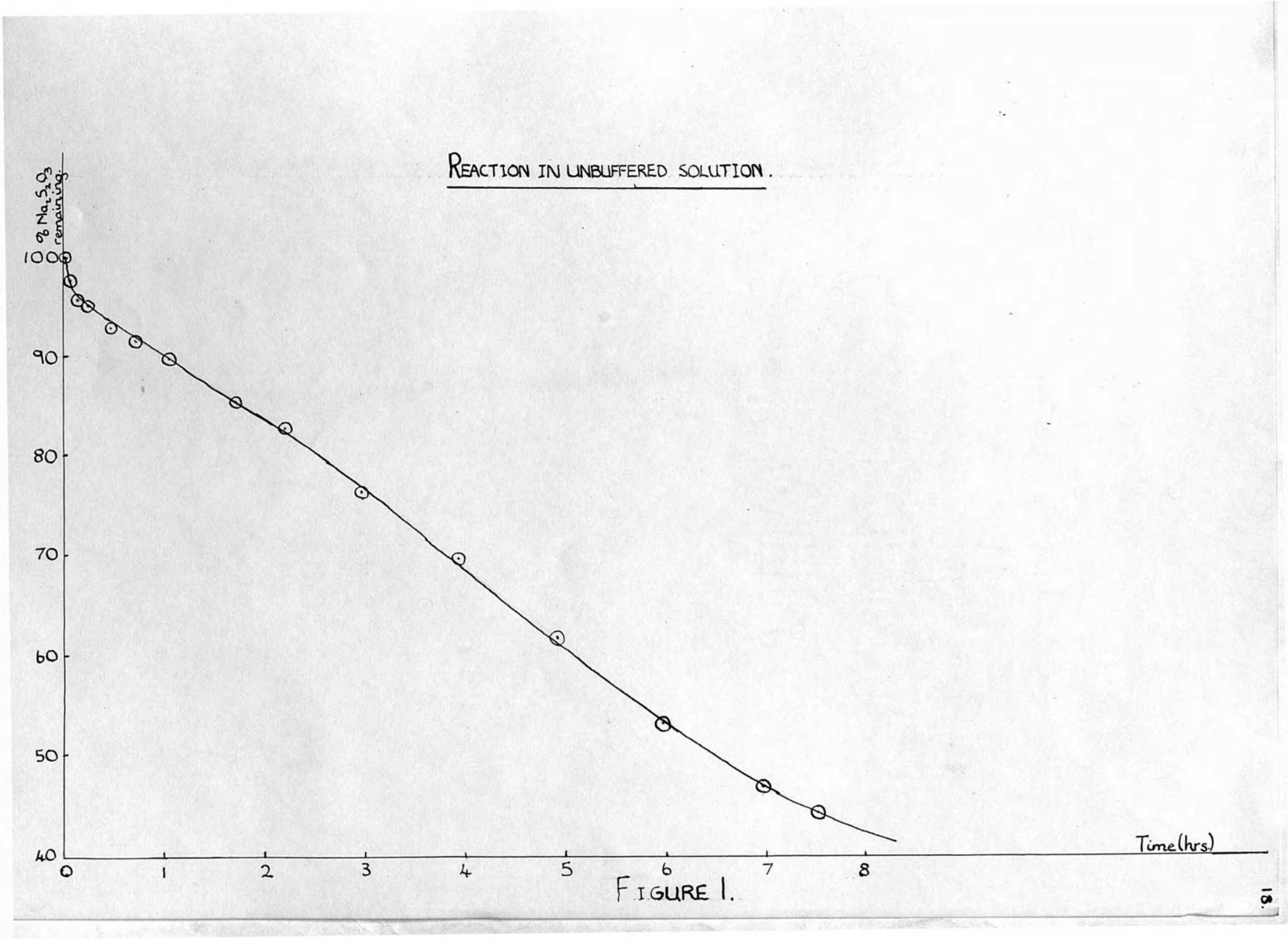

REACTION IN UNBUFFERED SOLUTION.
% $Na_2S_2O_3$ remaining
100
90
80
70
60
50
40
0
1
2
3
4
5
6
7
8
Time (hrs.)

FIGURE 1.

Thus at 30.0°C. the reaction proceeds rapidly for approximately the first twenty minutes; there is then a longer period of retardation followed by a further period of acceleration. This suggests a somewhat complex sequence of events during the course of the reaction. Hence the following series of experiments was carried out in order to investigate the possible causes of this acceleration - retardation pattern. In order to eliminate unnecessary complications the sodium thiosulphate and potassium ferricyanide were present in equimolecular quantities in the majority of experiments. The variation of the reaction rate with concentration ratio was however, also studied.
(See Chapter1. Section 2.10.)

(1) Effect of the purity of the potassium ferricyanide.

Although the purity of the potassium ferricyanide had been checked by titration (See Appendix 1.) it was decided to recrystallise a sample in case any of the compound had decomposed thereby causing the initial irregularities. The recrystallised ferricyanide was used in a kinetic run as before and the results showed no change in the general characteristics of the reaction. A graph of the results is shown in fig. 2. It was therefore deemed unneccessary to recrystallised this substance in future work.

Table 6.(1)

Reaction carried out with recrystallised potassium ferricyanide.

a = b = 0.02M. Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	5hrs.	0mins.	92.00
0	21	96.24	6	30	89.80
0	45	95.86	8	11	87.14
1	2	95.52	9	36	85.55
2	22	93.82	11	3	83.61
3	55	93.46			

REACTION USING RECRYSTALLISED

POTASSIUM FERRICYANIDE.

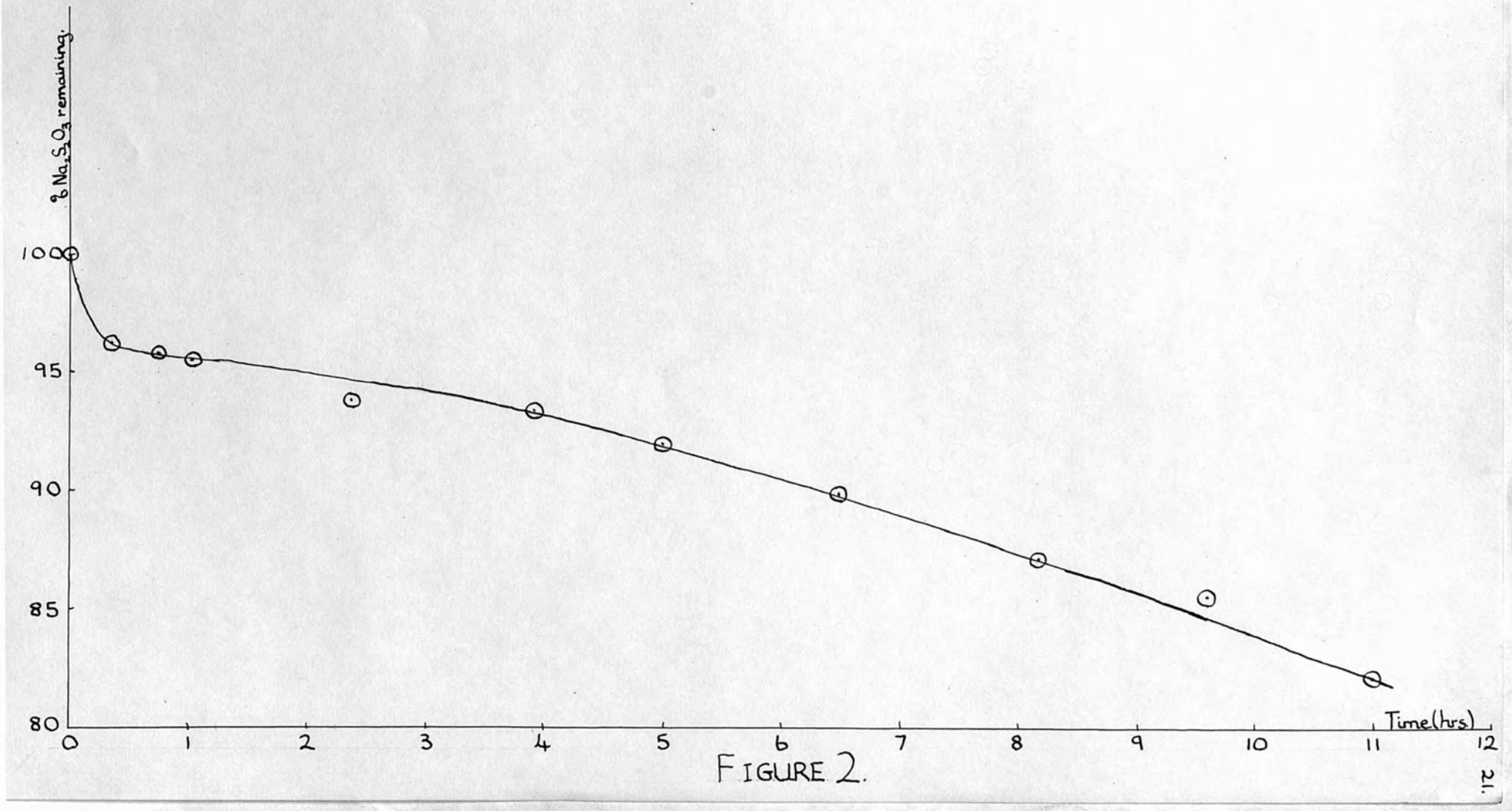


FIGURE 2.

(2) The effect of additions of potassium ferrocyanide.

The course of many chemical reactions is modified by the presence of the reaction products. Hence standard solutions of sodium thiosulphate, potassium ferricyanide and potassium ferrocyanide were mixed and maintained at 25.0°C. When the course of the reaction was followed in the usual way, it was found that the addition of potassium ferrocyanide had completely eliminated the initial period of rapid reaction. The general pattern now seemed to be a period of several hours of slow reaction, followed by acceleration to the usual rate for any given concentration and temperature. This effect is reminiscent of the observations made by Donnan and Le Rossignol in relation to the ferricyanide - iodide reaction, but it appears here in a much more acute form. Thus with the initial reactant concentrations each 0.0375M the time required for 10% change at 25.0°C. was 116min. in the absence of added ferrocyanide but 314min. when the solution was initially 0.0667M in this reagent, whereas the times required for 20% change were about 295min. and 430min. respectively, i.e. The second 10% of the change required 179min. in the former case but only 116min. in the latter. This apparent acceleration in the latter stages may be due to the increased ionic strength of the solution.

It was shown by varying the concentration of the ferrocyanide ion that addition of very small quantities of this substance (e.g. amounts equivalent to one tenth of the concentration of the sodium thiosulphate or potassium ferricyanide) do cause a considerable retardation during the initial stages of the reaction. (See Table 7.(1))

It can be seen from these results that with reactant concentrations of 0.025M the addition of sufficient ferrocyanide to make the initial solution 0.0025M in that reagent, increased the time for 10% change from 313min. to 428min. and the time for 20% change from 664min. to 791min. The later stages of the reaction, however, follow in each case much the same course as that of the reaction where no ferrocyanide has been added initially. Such an effect is to be anticipated since in the last experiments mentioned above, the ferrocyanide concentrations after the reaction was 20% complete were only in the ratio 2:3; hence its effect in the first mixture to which none had been added initially would be almost as great as in the second one which had a finite initial concentration of the compound.

Table 7.[1]

A comparison of the rates of reaction in the presence and absence of potassium ferrocyanide.

1A. a = b = 0.0375M. Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	10hrs.	2mins.	58.60
0	2	97.36	10	59	54.92
0	9	95.20	12	3	51.03
0	16	94.04	13	2	46.55
0	23	93.58	15	3	41.18
0	41	92.76	17	7	36.24
1	1	91.62	19	13	32.34
2	7	89.68	21	8	29.59
3	2	86.23	23	6	26.60
4	16	82.21	26	3	24.20
5	6	79.35	29	14	21.10
5	58	76.48	31	59	19.04
7	3	70.99	37	34	14.45
8	1	65.60	40	17	12.73
9	1	62.38	43	2	11.13
			45	1	9.17

Table 7[(i)] (contd.)

2A. a = b = 0.0375M. Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	17hrs.	4mins.	35.40
1	1	99.84	17	57	33.11
1	56	98.67	19	43	29.63
3	13	95.81	21	25	26.29
4	22	92.45	22	50	24.02
5	19	89.74	24	54	18.93
6	20	84.71	25	43	18.00
7	19	79.20	27	38	16.05
8	18	72.75	29	41	13.58
9	15	67.15	31	49	11.38
10	9	61.88	33	47	9.26
10	59	57.65	36	44	8.24
11	49	53.91	43	18	5.01
14	5	44.32	48	16	3.48
15	27	40.66			

c = Concentration of potassium ferrocyanide. = 0.0667M.

Table 7[(1)] (contd.)

1B. a = b = 0.025M. c = 0 Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	20hrs.	44mins.	60.07
0	23	95.60	23	5	54.65
1	15	95.16	24	49	51.06
2	4	93.76	26	49	46.39
3	32	91.36	28	43	42.81
5	2	90.38	31	18	41.07
6	31	87.36	33	50	36.50
7	32	86.60	36	18	34.65
9	17	83.43	38	58	31.62
12	3	78.21	40	48	29.23
13	55	73.23	42	56	27.27
15	33	69.65	44	52	26.94
16	54	66.26	46	11	25.74
19	9	62.03			

Table 7(i) (contd.)

2B. a = b = 0.025M. c = 0.0025M. Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	15hrs.	52mins.	72.16
0	42	98.60	17	28	69.15
1	21	97.90	18	53	65.59
1	58	96.91	20	31	61.34
2	59	95.56	22	6	58.07
3	60	94.44	25	28	51.55
4	59	93.58	27	24	47.66
6	2	91.92	29	56	42.38
7	3	90.10	32	56	37.95
7	59	88.97	36	2	35.53
9	43	85.95	39	19	30.24
11	32	82.04	42	3	29.63
12	46	81.10	44	56	26.69
14	22	76.94	46	59	25.04

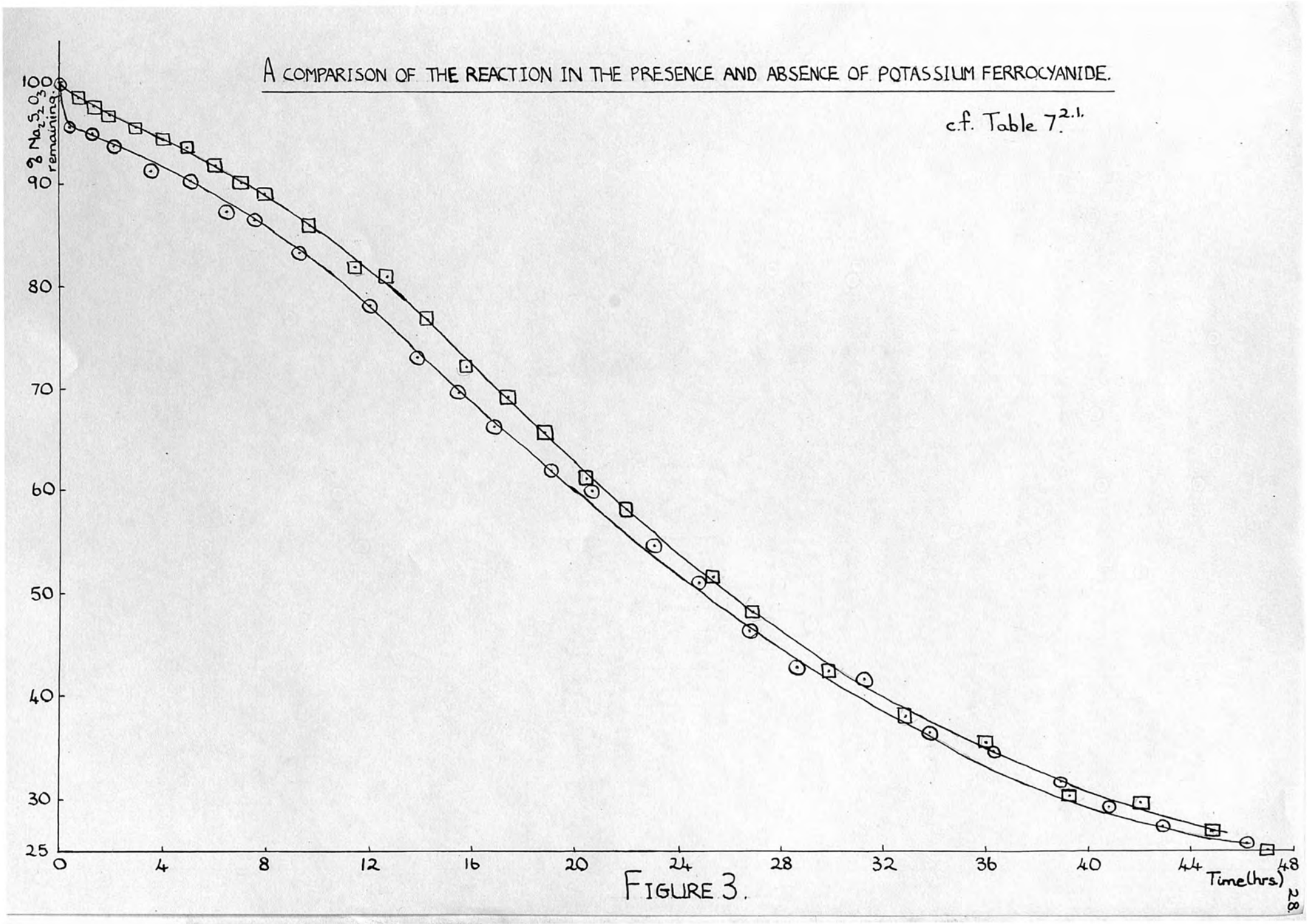

A COMPARISON OF THE REACTION IN THE PRESENCE AND ABSENCE OF POTASSIUM FERROCYANIDE.
c.f. Table 7.2.1.
% $Na_2S_2O_3$ remaining.
100
90
80
70
60
50
40
30
25
0
4
8
12
16
20
24
28
32
36
40
44
48
Time(hrs)

FIGURE 3.

(3) The effect of addition of cyanide ions.

Previous workers on the reactions of ferricyanides[1] have suggested that the complex ion is able under certain conditions, to lose a cyanide radical. In fact Donnan and Le Rossignol suggested rather tentatively, that both the ferricyanide and ferrocyanide ions tend to dissociate in this way and that the slowness of the reaction between ferricyanide and iodide ions was due to the reaction actually occurring between iodide ions and ferric ions obtained from such dissociation of the ferricyanide ion. This ion however, is very stable and consequently this dissociation can only occur to a small extent and it will be repressed strongly by small additions of cyanide ion. Hence if the reaction proceeded through the formation of ferric ions in the present case it would be likely that the addition of cyanide ions to the mixture of ferricyanide and thiosulphate ions would have a considerable influence on the course of the reaction.

A reaction involving ferric ions or any other species such as $Fe(CN)_5OH'''$ which may be formed by the partial hydrolysis of the ferricyanide ion, would be expected to be strongly retarded by the additions, whereas, of course, if the cyanide itself took any part in the reaction the addition of this ion would be expected to cause an acceleration.

It is known that cyanide ions react reversibly with

iodine to give cyanogen iodide.

$$I_2 + KCN \rightleftharpoons KI + CNI \qquad (3)$$

Thus if cyanide ions are added to the reaction mixture complications will arise in the estimation of the thiosulphate remaining.

When a very dilute solution of potassium cyanide was cooled to $0^{o}C.$ and titrated against standard iodine solution it was found that the reaction (3) proceeded to completion from left to right and that a given quantity of potassium cyanide always reacted with a constant quantity of iodine. Therefore it was possible to follow the course of the reaction in a mixture containing cyanide, thiosulphate and ferricyanide ions, in the usual manner, providing that an allowance was made for the volume of iodine reacting with the cyanide.

The concentration of potassium cyanide used in these experiments was very low because it is most unlikely that the potassium ferricyanide would dissociate to any great extent and also because of the practical difficulties involved in its use.

A typical set of results is given in Table 8.(1) and also Fig. 4. The additions appeared to have no appreciable effect on the character of the reaction curve and so probably the

reaction mechanism does not involve ionic species of the type $Fe(CN)_5OH'''$ or other ions produced by dissociation or hydrolysis of the ferricyanide ion.

Table 8.[1]

Reaction carried out in the presence of CN' ions.

Temperature 25.0°C.

a = b = 0.0375M. Concentration of KCN = 0.0002M.

Time.	% $Na_2S_2O_3$ remaining.	Time.	% $Na_2S_2O_3$ remaining.
0hrs. 0mins.	100.00	9hrs. 43mins.	52.80
0 30	94.01	11 23	46.88
0 56	91.69	14 34	41.06
1 18	89.87	17 7	33.76
2 24	86.25	19 15	28.79
3 34	82.83	20 52	26.56
4 49	74.35	23 3	22.75
6 35	66.43		
8 10	59.34		

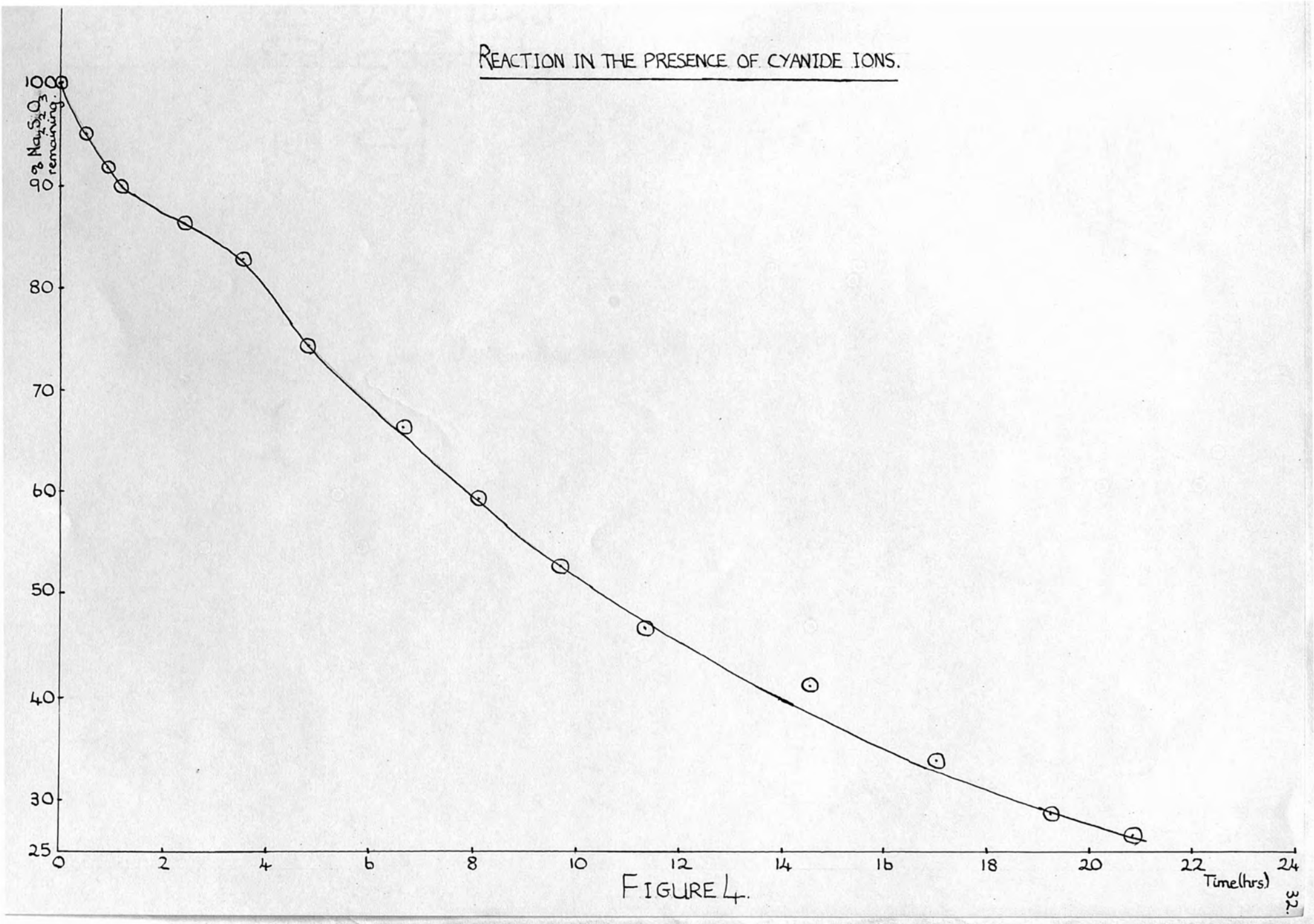

REACTION IN THE PRESENCE OF CYANIDE IONS.
% $Na_2S_2O_3$ remaining.
100
80
70
60
50
40
30
25
0
2
4
6
8
10
12
14
16
18
20
22
24
Time(hrs)

FIGURE 4.

(4) The effect of the addition of ferric ions.

As a further test as to whether a very small concentration of ferric ions might be present in the solution of potassium ferricyanide and hence influence the rate of the reaction, tests were made with added ferric ions.

Solutions of ferric chloride of different concentrations were prepared and added to the reaction mixture as before. Ferric chloride was chosen for this purpose in preference to other ferric compounds, as it was thought that the chloride ion was unlikely to cause any secondary effects. Formation of Prussian blue was negligible with the very small amounts of ferric ion involved.

Under these conditions the rate of the initial stages of the reaction did appear to be modified slightly. Some typical results are shown in Table 9[1] and Fig.4A. The relatively small effect observed, however, seems to preclude the possibility that the whole reaction mechanism proceeds through the intermediate formation of ferric ions.

Table 9.(1)

Reaction carried out in the presence of Fe^{+++} ions.

Temperature 25.0°C.

A. a = b = 0.0375M. Concentration of $FeCl_3$ = 0.0002M

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	8hrs.	1mins.	69.18
0	22	98.92	9	31	63.67
0	48	97.34	11	15	56.51
1	9	94.92	12	59	50.88
2	16	90.46	14	42	45.39
3	25	85.37	16	50	38.10
4	58	81.40	19	0	33.98
6	25	75.85	23	46	26.78

B. a = b = 0.03M. Concentration of $FeCl_3$ = 0.0003M

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	6hrs.	55mins.	84.81
0	18	98.96	9	16	80.39
0	40	98.50	10	56	76.87
1	0	97.10	12	26	71.86
2	8	94.30	14	30	68.46
3	37	91.84	15	55	62.86
5	8	88.80	18	32	55.61

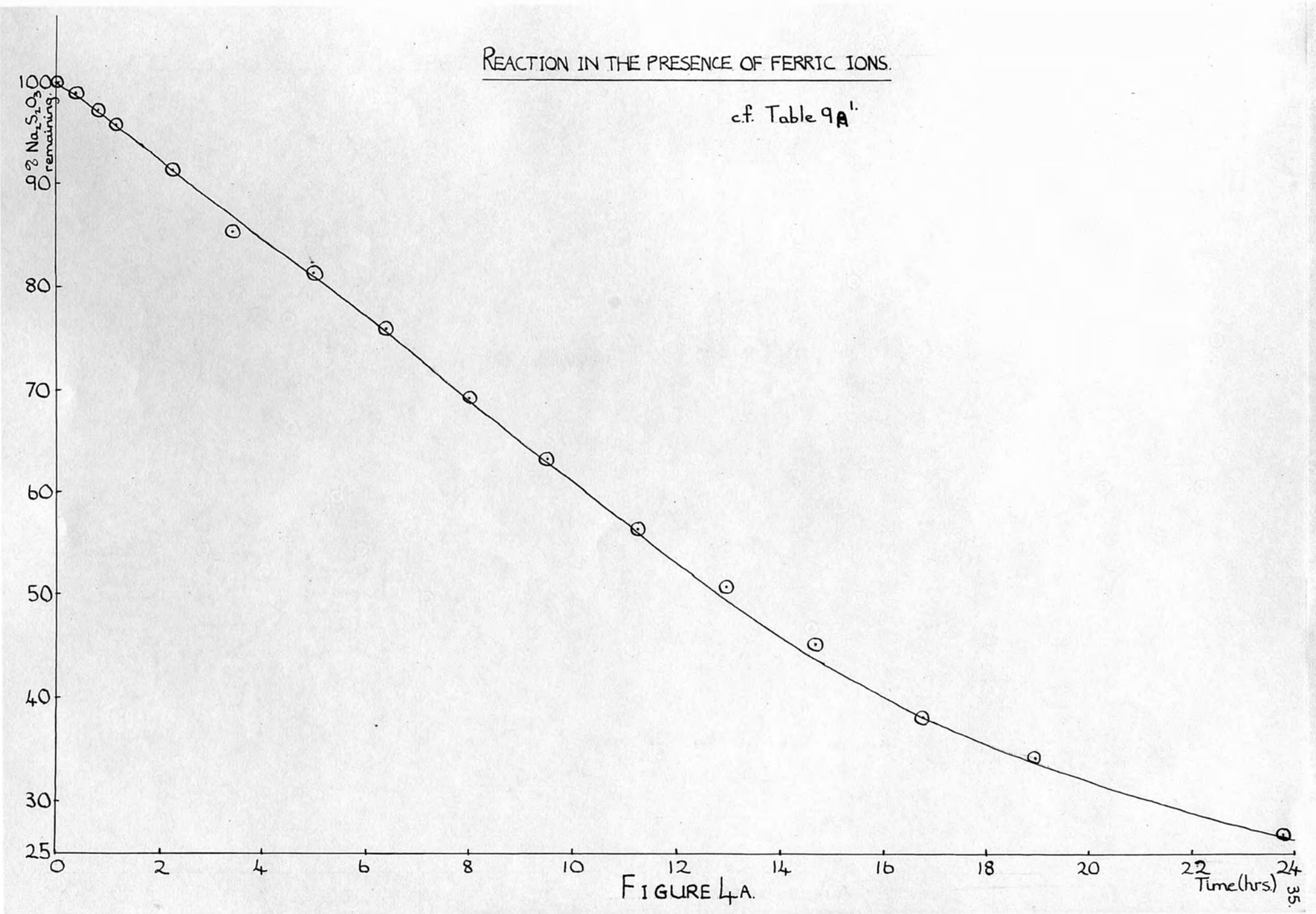

REACTION IN THE PRESENCE OF FERRIC IONS.
c.f. Table 9A'.
% $Na_2S_2O_3$ remaining.
100
90
80
70
60
50
40
30
25
0
2
4
6
8
10
12
14
16
18
20
22
24
Time (hrs.)

FIGURE 4A.

(5) The effect of dissolved oxygen.

The presence of dissolved oxygen in the solutions might have been causing the unusual character of the reaction curve in its initial stages. In this case, a pronounced difference in the reaction pattern would be expected if the experiments were carried out in an atmosphere of nitrogen.

Nitrogen was therefore bubbled through the sodium thiosulphate and potassium ferricyanide solutions for half an hour before they were mixed and the passage of nitrogen was continued during the kinetic run. The results obtained showed no appreciable change from those of an experiment carried out under normal conditions. Hence it was concluded that dissolved oxygen played no essential part in the reaction mechanism and was not responsible for the unusual form of the reaction curve. Some of the results obtained are shown in Table 10.[1] and Fig. 5.

Table 10.(1)

Reaction carried out in an atmosphere of nitrogen.

a = b = 0.0375M. Temperature = 25.0°C.

Time.	% $Na_2S_2O_3$ remaining.	Time.	% $Na_2S_2O_3$ remaining.
0hrs. 0mins.	100.00	7hrs. 59mins.	66.31
0 26	92.88	9 52	57.94
0 43	91.52	12 15	49.68
1 3	89.64	14 3	44.03
2 3	87.02	15 50	38.91
3 35	82.20	18 1	33.99
5 12	77.93	20 8	29.29
6 26	72.38	22 10	26.04

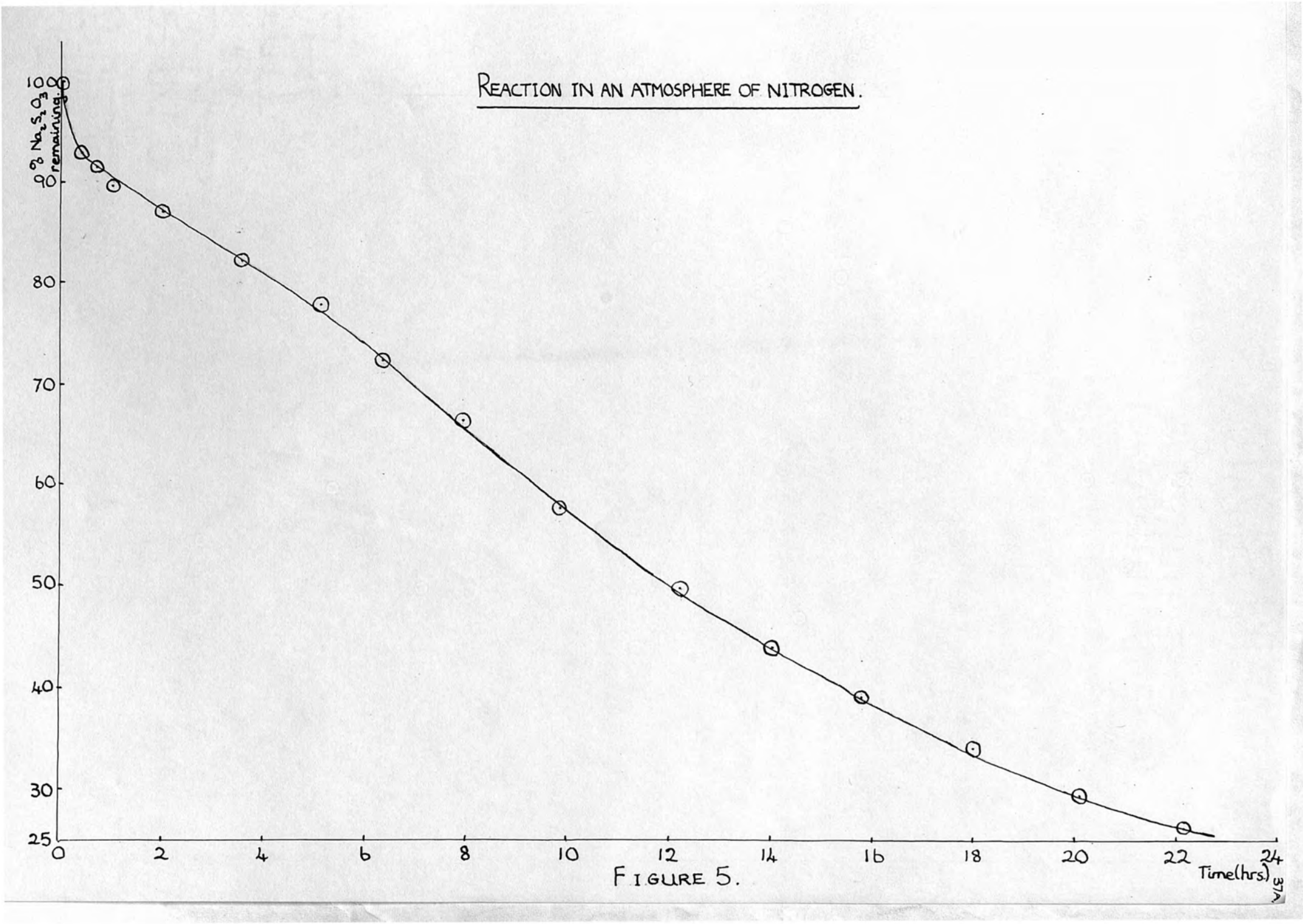

REACTION IN AN ATMOSPHERE OF NITROGEN.
% $Na_2S_2O_3$ remaining.
100
90
80
70
60
50
40
30
25
0
2
4
6
8
10
12
14
16
18
20
22
24
Time(hrs.)

FIGURE 5.

(6) The effect of pH on the course of the reaction.

A change in the pH of the solution during the reaction due to the difference between the dissociation constants of ferricyanic and ferrocyanic acids seemed a possible cause of the initial irregularities of the rate of the reaction. As a rapid method of determining whether or not a change in pH did affect the reaction, kinetic runs were carried out in the presence of sodium hydroxide solution. It was necessary to neutralise this before estimation of the residual sodium thiosulphate with iodine as these titrations are unsatisfactory in solutions of pH greater than 8; this is because iodide and hypoiodite are formed, the second of which is unstable and decomposes as shown in equation 5.

$$I_2 + 2\ OH^{'} = I^{'} + IO^{'} + H_2O \qquad (4)$$

$$3\ IO^{'} = 2\ I^{'} + IO_3^{'} \qquad (5)$$

Dilute hydrochloric acid was used for this purpose. It can be seen from the results shown in Fig.6 and Table 11[1] that small additions of sodium hydroxide do have a marked effect on the initial stages of the reaction.

In view of these results it was decided to carry out a series of experiments in buffered solutions. A mixture of solutions of disodium hydrogen phosphate and sodium dihydrogen phosphate was used for these trials, giving pH values of about 5.5, 6.2 and 7.5. (See Chapter 3. Section 3.)

It can be seen from Table 12[1] and Fig. 7 that the unusual features of the initial stages of the reaction are almost eliminated under these circumstances. Graphs of $\log_{10} p/p - x$ against t and also $1/p - x$ against t have been plotted;

p = Initial volume of standard $Na_2S_2O_3$ solution in mixture.

p - x = Volume of standard $Na_2S_2O_3$ solution in mixture after time t.

Some of these results are shown in Table 13[1] and Fig. 7. These seem to show that the reaction, at least in the region of pH just greater than 7, does obey a second order rate equation for the greater part of its course.

Table 11.(1)

Temperature 25.0°C.

a = b = 0.025M. Concentration of NaOH = 0.0003M.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	6hrs.	21mins.	74.76
0	22	98.50	7	43	72.15
0	40	96.52	9	18	66.86
1	2	94.32	10	58	63.14
1	17	92.12	13	8	58.85
1	33	90.80	14	21	55.00
1	40	91.34	15	32	52.26
2	5	88.82	17	35	46.99
3	19	84.21	18	38	44.47
4	52	78.71			

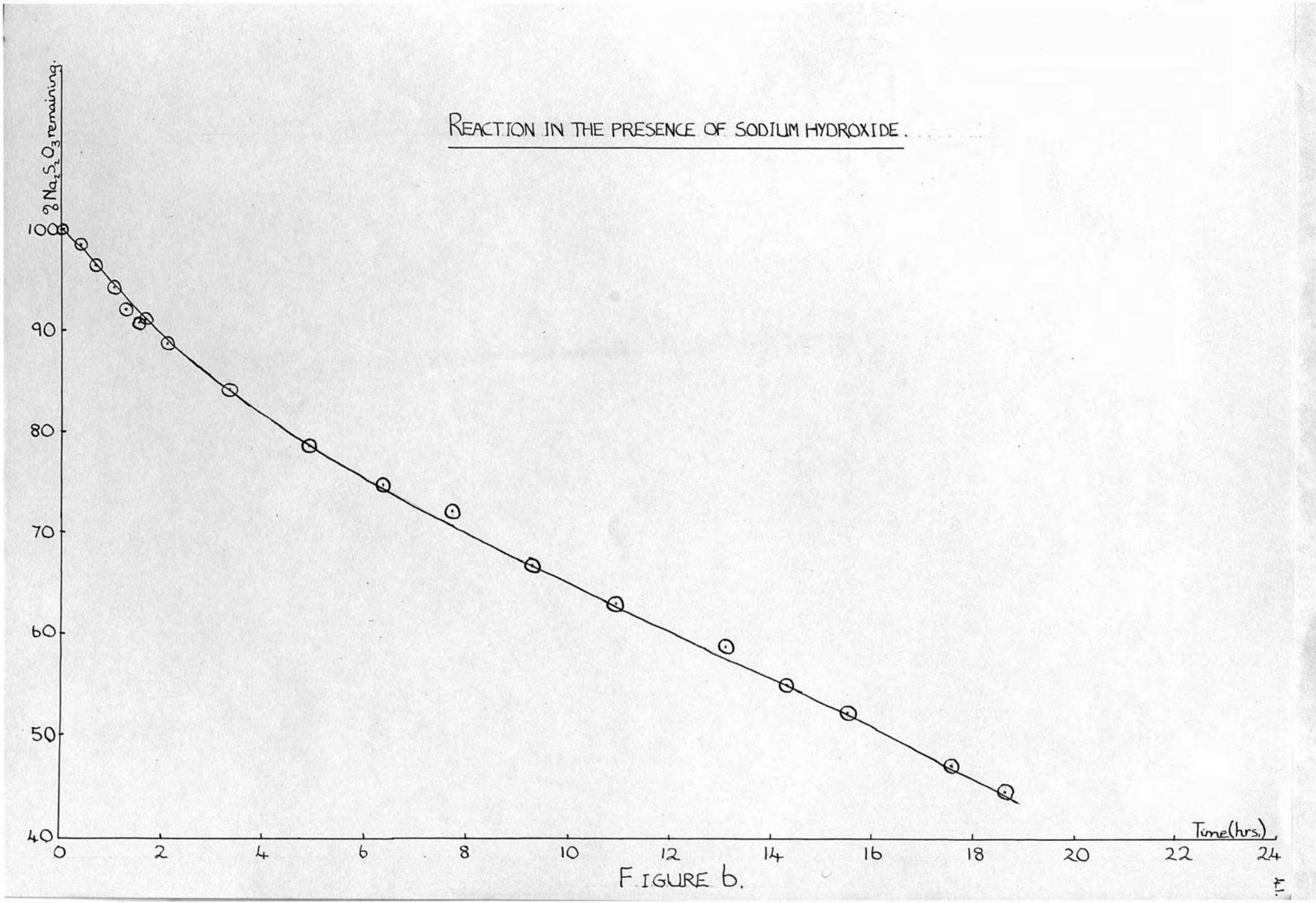

REACTION IN THE PRESENCE OF SODIUM HYDROXIDE.
% $Na_2S_2O_3$ remaining.
100
90
80
70
60
50
40
0
2
4
6
8
10
12
14
16
18
20
22
24
Time(hrs.)

FIGURE 6.

Table 12.(1)

Temperature = 25.0°C.

A. a = b = 0.03M. pH ≐ 7.5.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	10hrs.	49mins.	46.87
0	22	93.42	12	38	44.87
0	43	90.18	14	5	42.32
0	59	88.38	15	38	38.30
2	0	81.93	17	10	35.73
4	4	70.35	18	42	33.07
5	39	65.13	20	40	31.06
7	35	57.55	22	2	28.95
8	57	52.54	23	55	26.67

Table 12(1) (contd.)

Temperature = 25.0°C.

B. a = b = 0.03M. pH ≏ 5.5

Time.	% $Na_2S_2O_3$ remaining.	Time.	% $Na_2S_2O_3$ remaining.
0hrs. 0mins.	100.00	10hrs. 59mins.	49.00
0 22	93.36	12 39	45.91
0 42	90.84	13 59	42.00
1 2	88.60	15 27	37.63
2 11	84.10	17 10	33.56
3 34	75.97	18 35	29.76
4 57	71.75	19 49	27.67
6 35	64.44	21 39	23.58
8 0	58.74	23 14	21.20
9 34	53.64		

Table 12(1) (contd.)

Temperature = 25.0°C.

C. a = b = 0.0425M. pH ≏ 5.5

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	10hrs.	58mins.	27.27
0	25	91.50	12	37	26.33
0	44	88.18	14	0	21.38
1	2	85.95	15	31	18.87
1	57	77.71	17	1	16.18
3	39	65.03	18	38	13.96
4	58	55.35	20	56	11.73
6	33	46.15	22	5	11.42
7	51	39.17	23	3	9.83
9	2	34.42			

Table 12(1) (contd.)

Temperature = 25.0°C.

D. a = b = 0.0425M. pH ≐ 6.2

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	9hrs.	16mins.	42.35
0	24	92.82	11	8	40.77
0	44	89.84	12	48	33.05
1	11	87.08	14	3	29.97
2	6	81.33	15	43	26.63
3	36	73.11	17	15	23.55
5	12	63.61	18	51	20.97
6	46	53.62	20	14	19.59
8	8	47.39	21	22	18.30

Table 13.(1)

A. Temperature = 25.0°C.

a = b = 0.03M. pH ≏ 7.5.

Total volume of mixture = 130mls.

t mins.	(p -x)mls.	1/p - x mls.$^{-1}$	$\log_{10}$ p/p - x
0	7.69	0.13	0.00
120	6.27	0.16	0.09
240	5.41	0.18	0.15
360	4.77	0.21	0.21
480	4.24	0.24	0.26
600	3.79	0.26	0.31
720	3.42	0.29	0.35
840	3.15	0.32	0.39
960	2.93	0.34	0.42
1080	2.70	0.37	0.45
1200	2.52	0.40	0.48
1320	2.41	0.41	0.50

Table 13.[1] (cont.)

B. Temperature = 25.0°C.

a = b = 0.03M. pH ≏ 5.5

Total volume of mixture = 151mls.

t mins.	(p - x)mls.	$1/p - x$ mls.$^{-1}$	$\log_{10} p/p - x$
0	8.29	0.12	0.00
120	7.00	0.14	0.07
240	6.26	0.16	0.12
360	5.58	0.18	0.17
480	4.89	0.20	0.23
600	4.34	0.23	0.28
720	3.94	0.25	0.32
840	3.54	0.28	0.37
960	3.09	0.32	0.43
1080	2.66	0.38	0.49
1200	2.30	0.43	0.56
1320	1.89	0.53	0.64

Table 13.(i) (cont.)

C. Temperature = 25.0°C.

a = b = 0.0425M. pH ≃ 5.5

Total volume of mixture = 151mls.

t mins.	(p - x)mls.	1/p - xmls.$^{-1}$	$\log_{10}$ p/p - x
0	8.29	0.12	0.00
120	6.42	0.16	0.11
240	5.15	0.19	0.21
360	4.03	0.25	0.31
480	3.20	0.31	0.41
600	2.54	0.39	0.51
720	2.07	0.48	0.60
840	1.75	0.57	0.68
960	1.48	0.68	0.75
1080	1.23	0.81	0.83
1200	1.01	0.99	0.91
1320	0.87	1.15	0.98

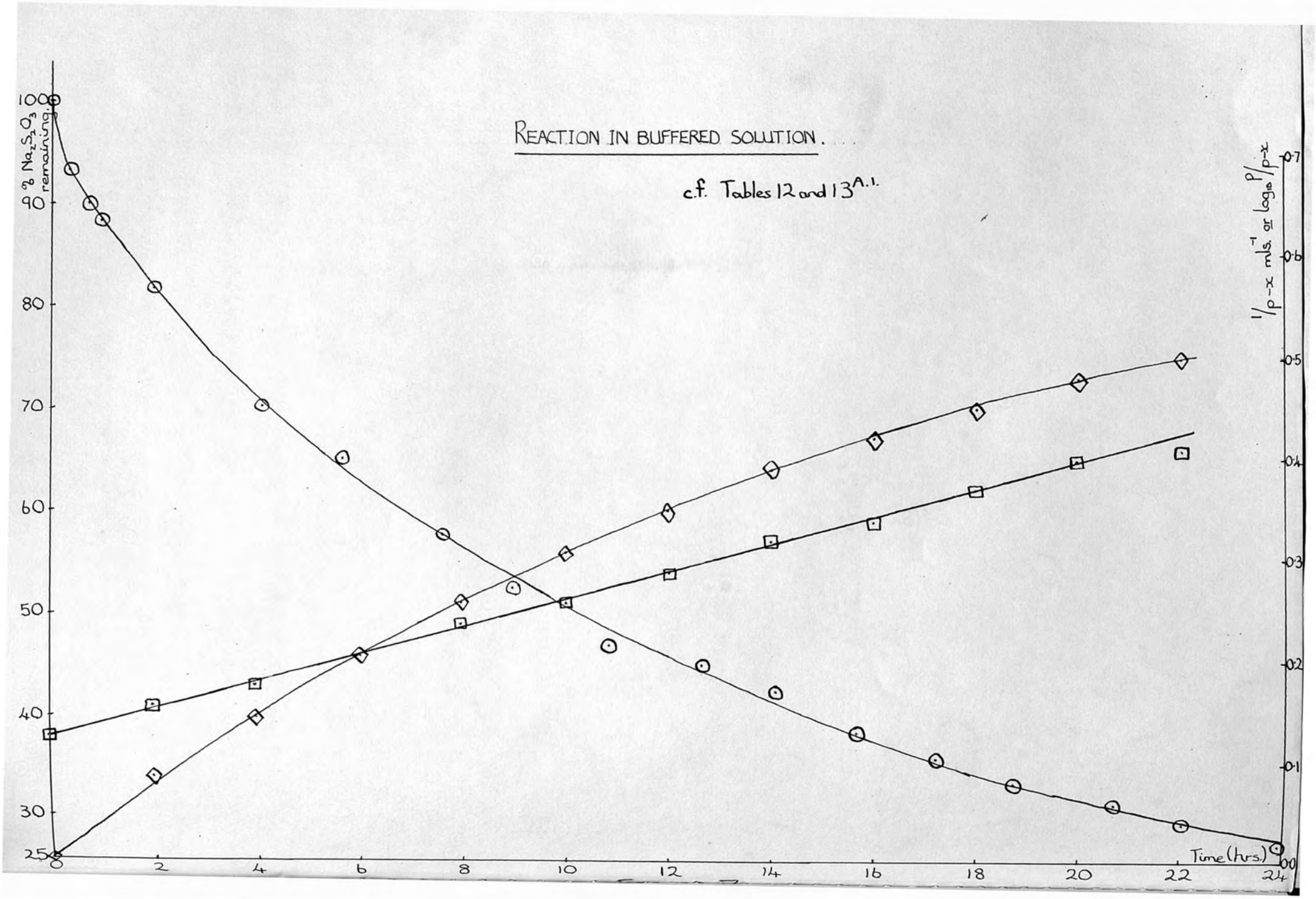
Table 13.(1) (contd.)

D. Temperature = 25.0°C.

a = b = 0.0425M pH ≃ 6.2

Total volume of mixture = 122mls.

t mins.	(p - x)mls.	$1/p - x$ mls.$^{-1}$	$\log_{10} p/p - x$
0	8.20	0.12	0.00
120	6.67	0.15	0.09
240	5.68	0.18	0.16
360	4.70	0.21	0.24
480	3.92	0.26	0.32
600	3.32	0.30	0.39
720	2.83	0.35	0.46
840	2.42	0.41	0.53
960	2.07	0.48	0.60
1080	1.80	0.56	0.66
1200	1.62	0.62	0.70


REACTION IN BUFFERED SOLUTION.
c.f. Tables 12 and 13 A.1.
% $Na_2S_2O_3$ remaining.
$1/p-x$ mls.$^{-1}$ or $\log_{10} p/p-x$
Time (hrs.)
100
90
80
70
60
50
40
30
25
0
2
4
6
8
10
12
14
16
18
20
22
24
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0

(7) A comparison of the methods for inhibiting side reactions during the determination of excess thiosulphate.*

The technique used by Sandved and Holte in the estimation of the residual sodium thiosulphate involved removal of a sample of the mixture and dilution, followed by addition of cadmium sulphate solution before titration with iodine. The cadmium ions served to check the disturbing reaction between iodine and ferrocyanide ions near the end point of the titration and also to prevent the reaction between ferricyanide and iodide ions. The cadmium sulphate should therefore serve the same purpose as the ice used in the present work.

A solution of cadmium sulphate ($3CdSO_4.8H_2O$) containing 23.6616g./ 250mls. of solution was prepared; 10mls. of this were added to the reaction mixture before titration of the residual thiosulphate. This quantity was in excess of the minimum necessary to precipitate all the ferricyanide and ferrocyanide ions present at any one time.

This method was compared with the standard one which had previously been adopted, by running comparative measurements on mixtures buffered to pH 6.97, the temperature

* It had not been possible at an earlier stage to obtain a copy of the paper written by Sandved and Holte[5] on this work, but when it became available it was decided to repeat certain of their experiments. Practical details of this work are given here but discussion of the comparable results is deferred until Chapter 4.

being raised to 35.0°C to accelerate the reaction.

It was found that the results obtained by the method involving the addition of cadmium sulphate coincided almost exactly with those from experiments where ice was used to prevent side reactions occurring during the titration. Some results obtained are shown in Table 14[(1)] and Fig.8.

Table 14.[(1)]

a b 0.0425M pH 6.97 Temperature 35.0°C.

* Cadmium sulphate solution added before titration.

Time.	% $Na_2S_2O_3$ remaining.	Time.	% $Na_2S_2O_3$ remaining.
0 hrs. 0 mins.	100.00	2 hrs. 23 mins.	56.56
0 9	95.44	*2 29	54.79
*0 13	91.51	3 4	50.59
0 22	89.76	*3 6	49.81
0 35	83.81	3 43	45.42
*0 38	80.37	*3 51	44.74
0 51	78.23	4 38	39.56
*0 55	75.20	*4 52	38.48
1 11	72.38	5 43	34.97
*1 13	70.53	*5 52	33.31
1 37	66.31	*6 48	30.18
*1 44	64.76	7 26	28.33
2 0	61.81	*7 46	28.13

GRAPH TO SHOW THE COMPARISON BETWEEN THE TWO METHODS

OF INHIBITING SIDE REACTIONS.

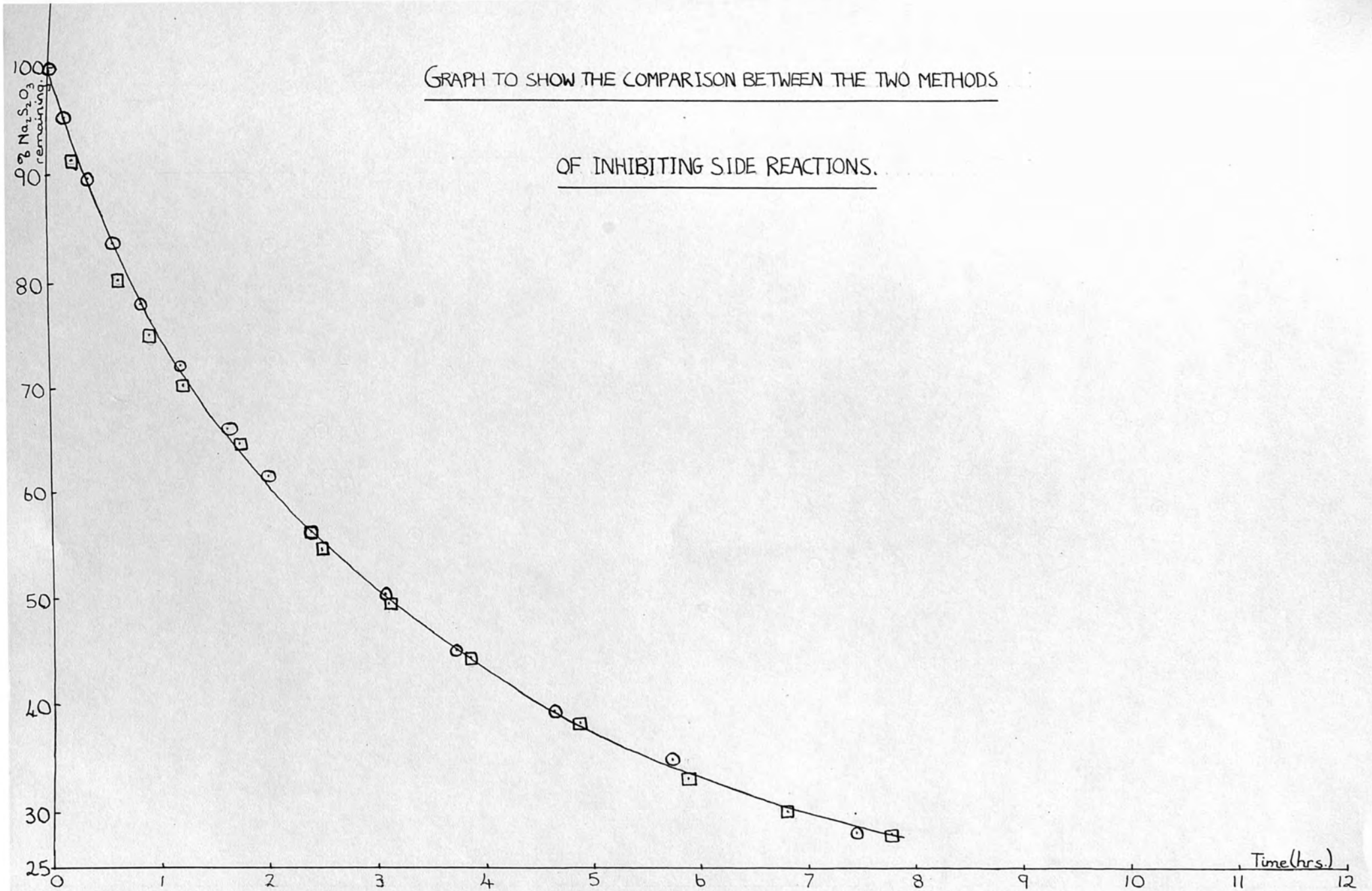


FIGURE 8.

(8) The effect of additions of potassium ferrocyanide to buffered mixtures.

The effect of these additions was first investigated qualitatively. It can be seen from these results that ferrocyanide ions have a considerable retarding effect on the reaction in solutions of pH varying from approximately 9.0 to 5.5 units. Some typical results are given in Tables 15(j). The buffer solutions used in these experiments are discussed in Chapter 3. Section 3. The inhibiting effect of the ferrocyanide ions appears to vary somewhat with the pH value and is greatest in slightly acid solutions.

Table 15(a)

a = b = 0.0425M c = 0.0046M pH = 9.0

Temperature = 35.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	2hrs.	4mins.	80.97
0	10	98.44	2	40	74.00
0	30	95.76	3	54	61.20
0	46	93.78	4	38	56.75
0	51	91.22	5	37	51.43
1	16	88.58	6	35	49.28
1	42	83.50	7	27	47.01

c = Concentration of potassium ferrocyanide.

Table 15(i)(b)

a = b = 0.0425M c = 0.0077M pH = 7.0

Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	10hrs.	38mins.	38.41
0	17	98.66	12	36	33.58
0	39	96.24	13	57	31.91
0	58	92.20	15	29	28.70
1	48	84.50	16	53	28.17
3	21	72.11	18	32	24.80
4	55	61.69	20	4	23.31
6	22	54.05	21	24	22.51
7	54	47.19	22	56	21.57
9	21	42.59			

Table 15(c)[1]

a = b = 0.03M c = 0.0015M pH = 6.2

Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	7hrs.	13mins.	87.60
0	25	97.50	10	1	80.90
0	57	97.00	12	32	74.90
1	48	95.16	13	57	71.35
3	56	92.72	16	53	62.43
5	34	90.40	18	34	57.42

Table 15(d)[1]

a = b = 0.03M c = 0.0063M pH = 6.2

Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	12hrs.	32mins.	74.78
0	26	99.09	13	56	70.50
0	59	98.60	15	35	66.10
1	48	98.24	17	13	60.73
3	57	93.92	18	42	54.85
5	44	91.26	20	19	49.67
7	23	87.96	21	50	46.80
10	1	81.61			

Table 15(i)(e)

a = b = 0.03M c = 0.0031M pH = 6.2

Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	10hrs.	41mins.	79.29
0	22	99.39	12	32	76.35
1	3	98.04	14	28	70.71
2	2	96.32	15	29	66.66
3	1	95.46	17	3	63.00
4	27	92.64	18	26	58.57
5	59	90.44	20	1	54.16
7	28	87.98	21	33	50.98
8	59	84.05	22	58	47.05

Table 15(i)(f)

a = b = 0.03M c = 0.0035M pH = 5.5

Temperature = 25.0°C.

Time.	% $Na_2S_2O_3$ remaining.	Time.	% $Na_2S_2O_3$ remaining.
0hrs. 0mins.	100.00	12hrs. 28mins.	71.25
0 57	97.00	14 0	66.54
2 0	95.70	15 31	62.27
3 34	92.22	16 59	56.58
5 1	89.80	18 26	51.69
6 34	87.62	19 58	47.20
7 56	83.51	21 25	43.70
9 31	79.71	22 54	39.51
10 56	74.91		

(9) The effect of additions of sodium tetrathionate to the buffered solutions.

The reaction between ferricyanide and thiosulphate ions leads to the formation of ferrocyanide and tetrathionate ions (Chapter 2. Section 2.) The effect of the addition of the latter to the initial reaction mixture is shown in Table 16[1] and Fig. 9. The method of preparation of the tetrathionate is given in Appendix 2.Some of these kinetic runs were carried out in reagent bottles covered with tin foil. (See Chapter 1. Section2.12.)

The results indicate that the presence of tetrathionate ions does have a considerable accelerating effect at the start of the reaction but during the later stages this is no longer noticeable. It was observed that the rate of reaction in the foil covered bottles was slightly lower than in those exposed to laboratory daylight, but the relative effects of the tetrathionate ions on the reaction rates under the two conditions seemed to be identical. Hence the accelerating effect of the tetrathionate did not appear to be associated specifically with the slight photochemical activation of the reaction.

Table 16.(1)

Comparison of reaction rates in the presence and absence of sodium tetrathionate.

a = b = 0.0425M pH = 8.21 Temperature = 35.0°C

1A. d = 0M			1B. d = 0.010M		
Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	Ohrs.	Omins.	100.00
0	6	91.26	0	4	91.02
0	10	88.34	0	10	83.87
0	16	83.73	0	16	78.69
0	31	75.95	0	31	68.80
0	46	70.21	1	6	54.31
1	2	64.00	1	53	43.59
1	15	61.20	2	25	36.52
1	30	57.32	3	33	32.19
1	50	51.21	4	34	28.53
2	7	47.84	5	53	24.66
2	41	42.39	7	15	23.75
3	13	37.69			
4	17	31.50			
5	25	29.33			
6	18	27.07			
7	12	24.72			

d = Concentration of sodium tetrathionate.

Table 16.[1] (contd.)

a = b = 0.0425M pH = 7.40 Temperature = 35.0°C.

2A. d = 0 2B. d = 0.0083M

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	Ohrs.	Omins.	100.00
0	3	96.62	0	7	90.00
0	13	91.40	0	16	82.03
0	23	85.35	0	27	75.03
0	42	77.07	1	4	57.72
1	0	69.58	1	36	48.84
1	32	61.51	2	3	44.33
2	0	55.48	2	45	40.18
2	42	48.49	3	45	34.50
3	42	40.08	4	48	30.46
4	36	36.62	5	34	28.45
5	33	32.83	6	31	24.89
6	29	30.36			

Table 16.[1] (contd.)

a = b = 0.0425M pH = 7.40 Temperature = 35.0°C.

(Foil covered bottles.)

3A. d = 0			3B. d = 0.012M		
Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	Ohrs.	Omins.	100.00
0	6	94.26	0	5	91.76
0	17	88.12	0	15	80.53
0	26	82.81	0	24	73.95
0	37	78.49	0	35	67.81
1	3	69.40	1	2	56.56
1	28	63.37	1	27	48.96
2	4	55.52	2	0	46.46
2	51	48.40	2	46	39.75
3	47	41.23	3	45	34.99
4	46	36.68	4	42	30.78
5	45	32.59	5	42	27.72
7	4	29.31	7	2	24.30

COMPARISON OF REACTION RATES IN THE PRESENCE AND ABSENCE OF SODIUM TETRATHIONATE.

c.f. Tables 16 A and B'.

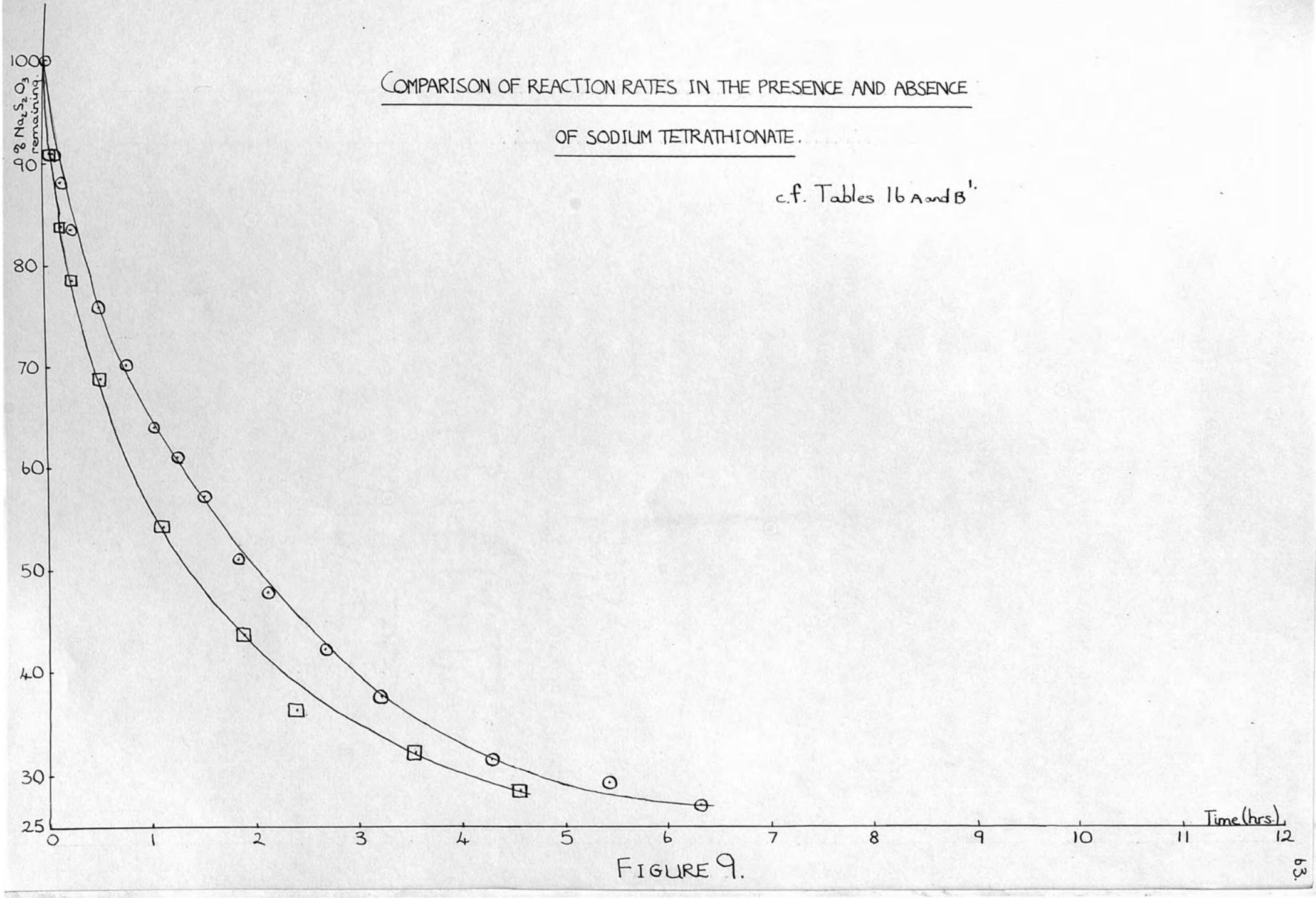


FIGURE 9.

(10) The effect of varying the concentration ratio of the reactants.

The experiments described in Section 6 of this chapter and also those to be described in Section 1 of Chapter 2, show that the reaction for a considerable range of pH values, is second order overall. This is in agreement with the conclusions of Sandved and Holte.[5] The following results support the view that the reaction is in fact first order with respect to both ferricyanide and thiosulphate ions. In this series of experiments the concentration of the former in the initial mixture was half that of the latter, thus ensuring that the thiosulphate was in ample excess throughout the reaction.

Considering a second order reaction of the type

$$A + B \longrightarrow \text{Products}$$

$$\text{then} \quad \frac{dx}{dt} = k(a-x)(b-x)$$

where x is the concentration of the product formed after time t, the initial concentration of one reactant is a and of the other is b and k is a velocity constant.

$$\text{Then} \quad kt = \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)}$$

which can be written in the form

$$k't = \log_{10}(a-x) - \log_{10}(b-x) + c$$

$$\text{where} \quad k' = \frac{a-b}{2.303} \quad \text{and} \quad c = \log_{10}\frac{b}{a}$$

If the reaction between ferricyanide and thiosulphate ions is of this type, then a graph of $\log_{10}(a-x)-\log_{10}(b-x)$ against t, should be a straight line. This proved to be the case as is shown in Table 17[(i)] and Fig.10.

Table 17.[(i)]

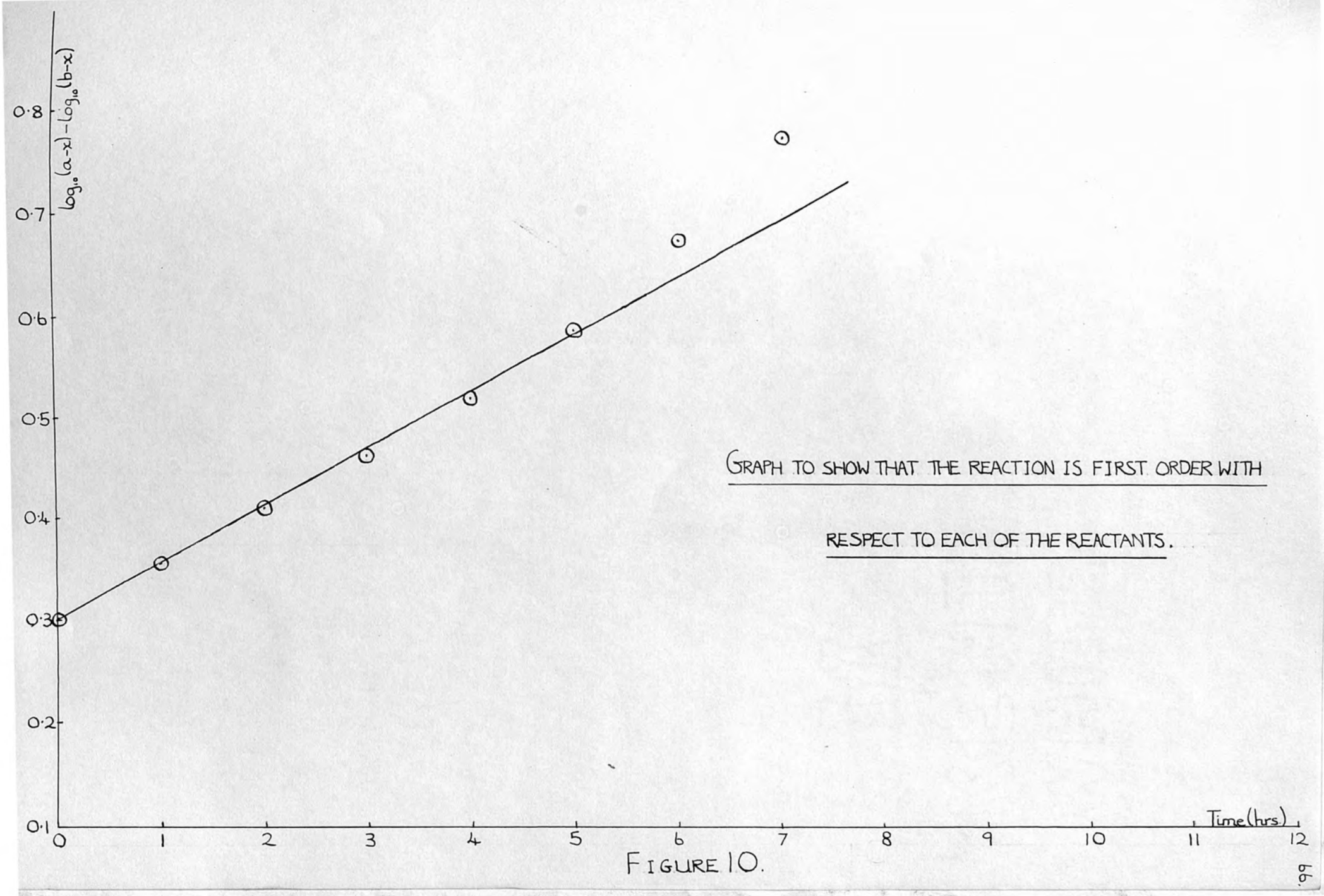
a = 0.0425M b = 0.0213M pH = 6.97 Temp. = 35.0°C.

A.

Time.	% $Na_2S_2O_3$ remaining.	Time.	% $Na_2S_2O_3$ remaining.
Ohrs. Omins.	100.00	2hrs. 37mins.	78.63
0 7	98.62	3 20	74.86
0 14	97.26	4 14	71.36
0 27	94.74	5 18	66.11
0 55	90.12	6 25	62.54
1 21	87.22	7 29	58.10
1 54	82.61		

B. The following readings were derived from results given above.

Time.	$\log_{10}(a-x)-\log_{10}(b-x)$	Time.	$\log_{10}(a-x)-\log_{10}(b-x)$
Ohrs.	0.3009	4hrs.	0.5200
1	0.3563	5	0.5879
2	0.4107	6	0.6771
3	0.4635	7	0.7745



GRAPH TO SHOW THAT THE REACTION IS FIRST ORDER WITH RESPECT TO EACH OF THE REACTANTS.

FIGURE 10.

(11) The effect of the ionic strength of the solution on the reaction rate.

The stoichiometric equation representing the reaction is

$$2\ S_2O_3^{''} + 2\ Fe(CN)_6^{'''} \rightleftharpoons S_4O_6^{''} + 2Fe(CN)_6^{''''} \qquad (6)$$

The evidence so far obtained however, indicates that the reaction is essentially of first order with respect to each reactant, giving it an overall order of two. It seems likely therefore, that the initial rate determining step may be a process of the type

$$Fe(CN)_6^{'''} + S_2O_3^{''} = Fe(CN)_6^{''''} + S_2O_3^{'}$$

Even if this is the case, it still involves reaction between highly charged ions and consequently would be expected to show a large primary salt effect,[8,9,10,11] i.e. the rate of the reaction should be considerably increased by the addition of neutral salts.

According to Brönsted's intermediate complex theory for a reaction of the type

$$A + B \longrightarrow C + D$$

it is assumed that the reactants are in equilibrium with an intermediate or transition state complex X.

i.e. $A + B \rightleftharpoons X \longrightarrow C + D$

$$\text{Reaction rate} = k[X] = k'[A][B]\frac{f_A f_B}{f_X}$$

where k is a velocity constant, k' is a constant and f_X etc. is the activity coefficient of X etc.

From the Debye-Huckel limiting law for an ion of charge z in an aqueous solution at 25°C

$$-\log f \simeq 0.5 z^2 \sqrt{\mu}$$

where μ is the ionic strength of the solution.

The primary salt effect will be determined by the term

$$f_A f_B / f_X$$

For reaction (6) this term is given by

$$\log f_A f_B / f_X = 6.0 \sqrt{\mu}$$

This suggests that a large positive primary salt effect should be observed.

Experiments were carried out in which solutions of potassium chloride of varying concentrations were added to the initial reaction mixture and it can be seen from some of the results given in Table 18[(1)] and Fig. 11, that these additions did in fact increase the reaction rate considerably.

The theory outlined above can only be applied quantitatively in solutions of low ionic strength. The ionic strength of solutions employed in the present work is normally high and so the theory has only been used to predict the type of effect that would be expected and which is in fact obtained.

Further experiments on this effect are described in Chapter 2. Section 2.4.

Table 18.(1)

Comparison of reaction rates at different ionic strengths.

a = b = 0.0425M pH = 6.97 Temperature = 35.0°C.

A. KCl = 0 μ = 0.40 B. KCl = 0.63M μ = 1.02

Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00
0	7	94.58
0	19	88.26
0	31	81.03
0	48	74.63
1	2	68.96
1	21	65.01
1	40	59.60
2	3	54.54
2	41	47.42
3	22	41.74

Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00
0	2	90.18
0	6	83.01
0	13	74.73
0	16	70.73
0	21	66.41
0	25	62.60
0	28	61.20
0	33	56.38
0	37	54.30
0	45	49.81
0	52	45.65
1	1	42.58

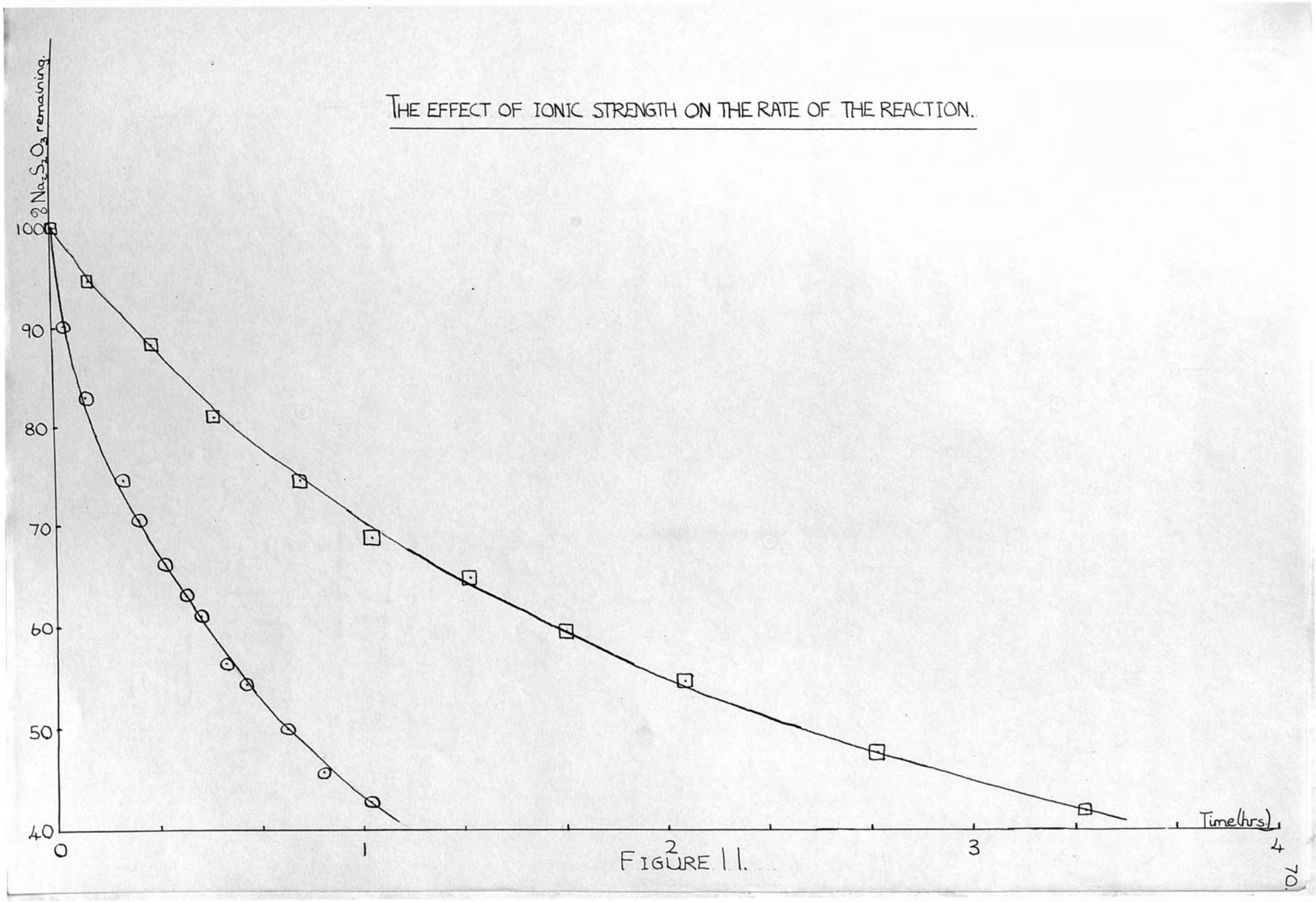

THE EFFECT OF IONIC STRENGTH ON THE RATE OF THE REACTION.
% $Na_2S_2O_3$ remaining.
100
90
80
70
60
50
40
0
1
2
3
4
Time(hrs.)

FIGURE 11.

(12) The effect of light on the reaction in buffered media.

Many of these reactions were followed for long periods of time e.g. 24hrs. The normal procedure in these cases was to follow the reaction for the first 12hrs., after which a second reaction mixture was prepared and left in the thermostat for twelve hours overnight, thus enabling the 12-24hr. period to be followed the next day. A slight break always appeared in the reaction curve at about 12hrs. and this was shown to be due to a small photochemical effect.

Experiments were carried out in bottles covered with tin foil. It was seen that over a range of pH values the reaction proceeded more slowly in the covered than in the uncovered bottles. These results are illustrated by a typical series shown in Table 19.(1) and Fig. 12. The general course of the reaction was however, unchanged, and as the effect was comparatively small the majority of the work was continued in uncovered bottles.

Table 19(i) (a)

a = b = 0.0425M pH = 5.53 Temperature = 35.0°C.

Reaction in covered bottles.

Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00
0	4	96.64
0	11	96.18
0	32	93.46
1	6	89.90
1	48	85.15
2	30	79.93
4	2	63.80
5	7	51.47
6	14	42.58
9	8	26.68

Reaction in uncovered bottles.

Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00
0	5	96.64
0	17	93.70
0	32	90.38
0	53	87.66
1	26	81.73
2	8	74.60
2	41	67.71
3	36	57.64
4	28	48.51
5	29	40.91
6	31	32.75
7	35	26.21

Table 19(1) (b)

a = b = 0.0425M. pH = 9.00 Temperature = 35.0°C

Reaction in covered bottles.			Reaction in uncovered bottles.		
Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	0hrs.	0mins.	100.00
0	4	96.00	0	7	95.06
0	10	93.52	0	17	91.70
0	27	90.44	0	32	87.34
0	51	87.48	0	51	84.95
1	15	82.04	1	12	80.80
1	57	76.84	1	44	75.83
2	22	75.30	2	15	72.10
3	14	67.38	3	6	63.79
4	23	59.94	4	3	55.64
5	42	52.04	5	2	51.89
6	54	48.12	6	12	47.94
8	3	44.80	7	4	45.35
			8	0	43.38

THE EFFECT OF LIGHT ON THE REACTION.

c.f. Table 19a'.

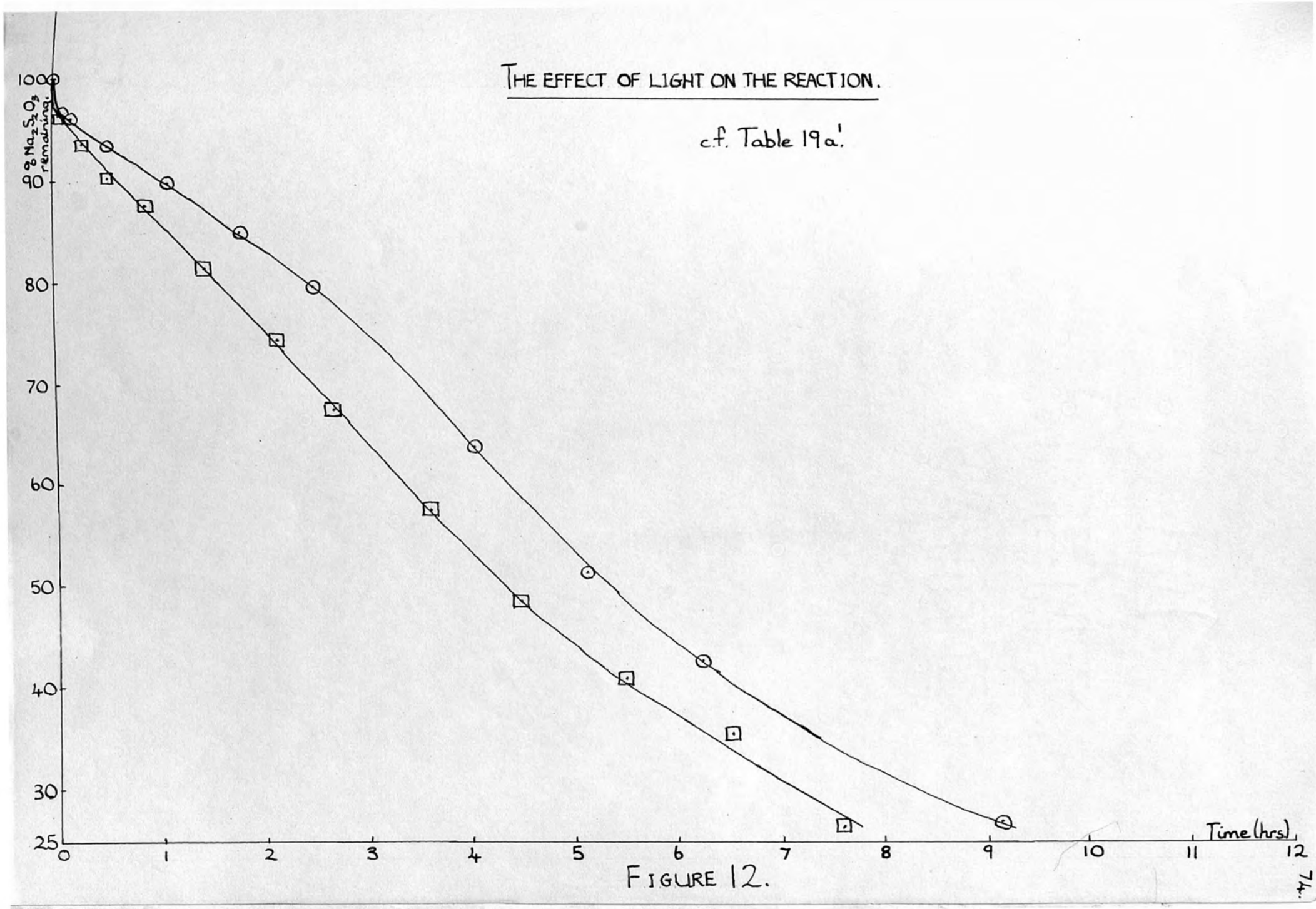


FIGURE 12.

CHAPTER 2.

THE REACTION BETWEEN FERRICYANIDE AND THIOSULPHATE IONS IN BUFFERED SOLUTION.

Section 1.

An investigation of the order of the reaction.

The experiments described in this section were carried out in order to investigate, in greater detail, the effect of buffering the reaction mixture at different pH values. The rates of the reactions were followed by titration of the residual thiosulphate in the mixtures, with iodine, as described in Chapter 1. Section 1. Measurements were made at 25.0°C and 35.0°C, using mixtures buffered to pH values ranging from 5.5 to 9.0 units. Details of the buffer mixtures used are given in Chapter 3. Section 3.

This work shows that the velocity of the reaction does vary considerably with the pH value at which the mixture is buffered. A maximum velocity seems to be reached in the region of pH 8, with a considerable fall from this value at both higher and lower pH values.

One experiment was performed at a pH value of approximately 11 units and in this case the form of the reaction curve differed entirely from results obtained in less alkaline solutions. An induction period of about eleven hours preceded a reaction with a half life period of four hours and twenty minutes.

Graphs have been plotted of $1 / p-x$ and $\log_{10} p / p-x$ against t, where p is the initial concentration of the

reactants, (in all these experiments this is the same for both sodium thiosulphate and potassium ferricyanide) x is the concentration of ferrocyanide formed and t is the time. Throughout the pH range 9 - 7, the graph of 1 / p-x against t is a straight line over the greatest part of the reaction, but in more acid solutions a better straight line is obtained by plotting $\log_{10}p$ / p-x against t.

These results suggest that the reaction does follow a second order law over a considerable part of its course when the solution is neutral or slightly alkaline. From measurements at 20°C and at pH 6.1, obtained by using a phosphate buffer similar to that employed in the present work Sandved and Holte[5] also inferred that the primary reaction is of second order. They suggested, however, that it must be subject to pronounced disturbing influences because calculations of the reaction order using the formula of Noyes and van't Hoff, gives values ranging from 1.82 to 2.22 with a mean value of 2.16. This pH value, however, lies within the range where the present work indicates departure from second order kinetics.

Slight deviations from second order behaviour were invariably found immediately after the start of the reaction, but these deviations were much smaller than those described by Sandved and Holte. Also, towards the end of the reaction the values of 1 / p-x became less than would be expected

for a second order process, but this effect was not observed at such early stages of the reaction as had been indicated by Sandved and Holte. The apparent departure from second order kinetics under such conditions, can be readily accounted for by the reaction not going quite to completion or becoming very slow indeed in the final stages. Evidence of this was obtained through there being always a small but finite residual amount of thiosulphate which could be titrated with iodine, even after the reaction mixture containing equivalent initial amounts of ferricyanide and thiosulphate had been allowed to stand for several days. Under such circumstances, however, the determination of the equilibrium state of the reaction, if such existed, could not be carried out with certainty as small traces of sulphur always appeared after the reaction products had been kept for more than a day or two.

The fact that Sandved and Holte's measurements suggested that the equilibrium was reached at a smaller percentage reaction than in the present work may be associated with the high ionic strength at which they worked.

Although the majority of Sandved and Holte's experiments were carried out in buffer solutions giving pH 6.1 under the experimental conditions, a few of their kinetic studies were also made at pH 3.0, using the citrate buffer mixtures recommended by Mc Ilvaine.[18] According to Scheffer and Bohm[20]

the thiosulphate ion begins to decompose as shown below at pH values of 4.6 and below.

$$S_2O_3^{''} + H^{+} = HS_2O_3^{'}$$

$$HS_2O_3^{'} = HSO_3^{-} + S$$

$$6\ H^{+} + 5\ S_2O_3^{''} = 2\ S_5O_6^{''} + 3\ H_2O$$

Holluta and Martini[19] on the contrary, inferred that the rate of decomposition of the thiosulphate ion is negligable even down to pH 3.0.

As these results suggest that the experiments which Sandved and Holte performed at pH 3.0 may have been complicated by the formation of free sulphur and of higher thionates, the following experiments were carried out to gain an approximate idea of the probability of sulphur formation under these conditions.

Mixtures of 5mls.of 0.2M disodium hydrogen phosphate solution and 15mls. of 0.1M citric acid solution, were prepared, giving buffer solutions of pH 3.2. 50mls. of sodium thiosulphate solution and 50mls. of water were added to one mixture, and 50mls. of sodium thiosulphate solution and 50mls.of potassium ferricyanide solution to the other. These solutions were prepared so that the final mixtures were 0.0425M in sodium thiosulphate and / or potassium ferricyanide. All the solutions were brought to 35.0°C

before mixing and were maintained at this temperature.

In the first mixture, which was colourless, a trace of sulphur was observed after three minutes and clouds of sulphur had appeared after nine minutes. No effects were visible in the second case until after two hours, the yellow solution turned distinctly green, presumably due to the presence of colloidal sulphur.

Therefore, although the work of Sandved and Holte was carried out at 20.0°C, it does seem likely that the presence of sulphur, due to the decomposition of the sodium thiosulphate, may have interfered with the experiments at pH 3.0.

Table 1 (a)[2]

a = b = 0.0425M pH = 5.53 Temperature = 25.0°C

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	11hrs.	1mins.	43.14
0	15	94.62	12	26	39.22
0	35	91.64	13	57	35.30
0	58	89.86	15	28	31.86
1	57	86.77	17	10	27.22
3	25	80.35	18	45	25.20
5	2	72.74	20	13	22.34
6	36	64.07	21	44	20.33
8	2	56.57	23	12	18.78
9	32	49.33			

Table 1 (b)

a = b = 0.0425M pH = 5.53 Temperature = 25.0°C

Total volume of mixture = 110mls.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
0hrs.	9.10mls.	0.000	0.110mls^{-1}
1/4	8.66	0.022	0.115
1/2	8.43	0.034	0.118
3/4	8.27	0.041	0.121
1	8.17	0.057	0.122
2	7.87	0.063	0.127
3	7.51	0.084	0.133
5	6.64	0.137	0.151
7	5.65	0.207	0.177
9	4.71	0.296	0.212
11	3.93	0.365	0.255
13	3.42	0.425	0.292
15	2.98	0.485	0.336
17	2.56	0.551	0.391
19	2.23	0.611	0.448
21	1.95	0.669	0.513

Between t = 9hrs. and t = 19hrs. $\log_{10}$ p / p-x is linear with slope 0.0321hrs.$^{-1}$ This corresponds with $k_1 = 8.912 \times 10^{-6}$ sec.$^{-1}$.

Table 2 (a)[2]

a = b = 0.0425M pH = 5.53 Temperature = 35.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	2hrs.	41mins.	67.71
0	5	96.64	3	36	57.64
0	17	93.70	4	28	48.51
0	32	90.38	5	29	40.91
0	53	87.66	6	31	32.75
1	26	81.73	7	35	26.21
2	8	74.60			

Table 2 (b)[2]

a = b = 0.0425M pH = 5.53 Temperature = 35.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
Ohrs.	9.10mls	0.000	0.110mls^{-1}
1/4	8.58	0.026	0.117
1/2	8.29	0.041	0.121
3/4	8.08	0.052	0.124
1	7.87	0.063	0.127
2	6.89	0.121	0.145
3	5.83	0.193	0.172
4	4.87	0.272	0.205
5	4.05	0.352	0.247
6	3.31	0.439	0.302
7	2.69	0.529	0.372

Between t = 1hr. and t = 5hrs. $\log_{10}$ p / p-x is linear with slope 0.0695 hrs.$^{-1}$ This corresponds with $k_1 = 1.930 \times 10^{-5}$ sec^{-1}

Table 3 (a)[2]

a = b = 0.0425M pH = 6.25 Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	9hrs.	51mins.	44.86
0	25	91.60	11	16	40.10
0	45	89.95	12	38	35.81
1	11	87.80	14	3	33.55
2	7	82.33	15	31	30.34
3	11	78.05	17	29	26.42
4	52	69.48	19	14	23.44
6	37	59.60	20	54	21.89
8	17	50.92	22	32	19.75

Table 3 (b)[2]

a = b = 0.0425M pH = 6.25 Temperature = 25.0°C.

Time.	(p-x)	$\log_{10}$p / p-x	1 / p-x
0hrs.	9.10mls.	0.000	0.110mls^{-1}
1/4	8.50	0.030	0.118
1/2	8.29	0.040	0.121
1	8.05	0.053	0.124
2	7.59	0.079	0.132
3	7.13	0.106	0.140
5	6.22	0.165	0.161
7	5.22	0.241	0.192
9	4.35	0.321	0.230
11	3.71	0.390	0.270
13	3.22	0.451	0.311
15	2.84	0.506	0.352
17	2.49	0.563	0.402
19	2.20	0.617	0.455
21	1.97	0.665	0.508

Between t = 3hr. and t = 13hrs. $\log_{10}$ p/p-x is linear with slope 0.0347hrs.$^{-1}$ This corresponds with $k_1 = 9.638_{x10}{}^{-6}$sec^{-1}

Table 4 (a)[2]

a = b = 0.0425M pH = 6.25 Temperature = 35.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	2hrs.	23mins.	64.42
0	6	95.36	3	11	56.16
0	13	93.45	4	11	47.21
0	27	88.20	5	21	39.20
0	44	84.62	6	33	32.38
1	24	75.89	7	28	29.04

Table 4 (b)[2]

a = b = 0.0425M pH = 6.25 Temperature = 35.0°C.

Time.	(p-x)	$\log_{10} p / p-x$	1 / p-x
0hrs.	9.10mls.	0.000	0.110mls^{-1}
1/4	8.37	0.036	0.120
1/2	7.98	0.057	0.125
3/4	7.65	0.076	0.131
1	7.35	0.093	0.136
2	6.24	0.164	0.160
3	5.27	0.237	0.190
4	4.43	0.313	0.226
5	3.75	0.385	0.267
6	3.24	0.449	0.309
7	2.81	0.510	0.356

Between t = 2hrs. and t = 5hrs. $\log_{10}$ p/p-x is linear with slope 0.0763hrs.$^{-1}$ This corresponds with $k_1 = 2.120 \times 10^{-5}$ sec^{-1}

Table 5 (a)[2]

a = b = 0.0425M pH = 6.97 Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	10hrs.	33mins.	35.06
0	7	96.44	12	42	30.99
0	28	90.98	14	0	29.20
0	52	85.38	15	34	26.72
1	54	75.05	16	54	25.02
3	23	64.35	18	31	23.41
5	2	54.95	19	51	22.74
6	23	48.04	21	22	20.85
7	58	43.12	22	53	20.66
9	26	38.19			

Table 5 (b)[2]

a = b = 0.0425M pH = 6.97 Temperature = 25.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
0hrs.	9.10mls.	0.000	0.110mls^{-1}
1/2	8.15	0.048	0.123
1	7.63	0.077	0.131
1 1/2	7.17	0.104	0.140
2	6.79	0.127	0.147
4	5.55	0.215	0.180
6	4.61	0.296	0.217
8	3.90	0.368	0.256
10	3.34	0.436	0.299
12	2.93	0.495	0.343
14	2.62	0.541	0.382
16	2.35	0.588	0.426
18	2.15	0.627	0.465
20	1.98	0.663	0.505
22	1.85	0.692	0.541

Between t = 0hrs. and t = 10hrs. 1 /p-x is linear with slope 0.0182. This corresponds with $k_2 = 2.362 \times 10^{-8}$ moles.secs.$^{-1}$ litres^{-1}

Table 6 (a)[2]

a = b = 0.0425M pH = 6.97 Temperature = 35.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	2hrs.	23mins.	56.56
0	9	95.44	3	4	50.59
0	22	89.76	3	43	45.42
0	35	83.81	3	50	44.14
0	51	78.23	4	38	39.56
1	11	72.38	5	43	34.97
1	37	66.31	6	50	30.57
1	44	64.76	6	55	30.09
2	0	61.81	7	26	28.33

Table 6 (b)[2]

a = b = 0.0425M pH = 6.97 Temperature = 35.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
Ohrs.	9.10mls.	0.000	0.110mls^{-1}
1/2	7.80	0.066	0.128
1	6.91	0.119	0.145
2	5.53	0.216	0.181
3	4.63	0.293	0.216
4	3.97	0.360	0.252
5	3.48	0.417	0.287
6	3.07	0.471	0.326
7	2.71	0.526	0.369

Between t = Ohrs. and t = 5hrs. 1 / p-x is linear with slope 0.0354.

This corresponds with $k_2 = 4.593 \times 10^{-8}$ moles.secs.$^{-1}$ litres.$^{-1}$

Table 7 (a)[2]

a = b = 0.0425M pH = 7.21 Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	10hrs.	57mins.	29.50
0	12	94.61	12	39	30.23
0	33	89.14	14	3	28.04
0	52	84.22	15	27	26.31
1	53	74.03	16	59	24.22
3	27	61.38	18	31	22.95
5	0	52.18	20	3	21.76
6	29	45.43	21	35	20.03
8	0	39.52	23	5	19.58
9	31	35.06			

Table 7 (b)[2]

a = b = 0.0425M pH = 7.21 Temperature = 25.0°C.

Time.	(p-x)	$\log_{10}$ p/ p-x	1 / p-x
Ohrs.	9.10mls.	0.000	0.110mls^{-1}
1/4	8.40	0.035	0.119
1/2	8.05	0.054	0.124
1	7.51	0.083	0.133
2	6.57	0.141	0.152
4	5.26	0.238	0.190
6	4.31	0.324	0.232
8	3.57	0.406	0.280
10	3.14	0.462	0.319
12	2.80	0.512	0.357
14	2.52	0.558	0.397
16	2.28	0.601	0.439
18	2.10	0.637	0.476
20	1.96	0.667	0.510

Between t = Ohrs. and t = 16hrs. 1 / p-x is linear with slope 0.0206.

This corresponds with $k_2 = 2.668 \times 10^{-8}$ moles.secs.$^{-1}$litres.$^{-1}$

Table 8 (a)[2]

a = b = 0.0425M pH = 7.21 Temperature = 35.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	2hrs.	55mins.	48.99
0	8	95.20	3	44	42.56
0	16	91.75	4	29	38.35
0	28	84.56	5	11	35.47
0	46	77.94	6	17	31.35
1	10	70.18	6	44	29.91
1	40	63.18	8	4	26.18
2	21	54,46			

Table 8 (b)[2]

a = b = 0.0425M pH = 7.21 Temperature = 35.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
Ohrs.	9.10mls.	0.000	0.110mls.$^{-1}$
1/2	7.69	0.073	0.130
1 1/2	6.72	0.132	0.149
2	5.93	0.186	0.169
3	5.32	0.233	0.188
4	4.41	0.315	0.227
5	3.74	0.386	0.267
6	2.93	0.442	0.304
7	2.63	0.492	0.341
8	2.40	0.539	0.380
		0.579	0.417

Between t = Ohrs. and t = 8hrs. 1 / p-x is linear with slope 0.0384.

This corresponds with $k_2 = 4.982 \times 10^{-8}$ moles.secs.$^{-1}$litres.$^{-1}$

Table 9 (a)[2]

a = b = 0.0425M pH = 7.40 Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	8hrs.	14mins.	36.66
0	21	92.21	9	45	32.01
0	41	87.09	11	11	28.56
1	6	82.33	17	24	23.56
2	3	74.36	19	9	20.11
3	8	65.68	20	48	19.64
4	48	54.97	22	24	17.62
6	33	44.98			

Table 9 (b)[2]

a = b = 0.0425M pH = 7.40 Temperature = 25.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
Ohrs.	9.10mls.	0.000	0.110mls.$^{-1}$
1/4	8.52	0.029	0.117
1/2	8.15	0.048	0.123
1	7.60	0.078	0.132
2	6.78	0.128	0.148
3	6.07	0.176	0.165
5	4.87	0.272	0.205
7	3.85	0.374	0.260
9	3.10	0.468	0.323
11	2.65	0.536	0.377
13	2.37	0.584	0.422
15	2.18	0.621	0.459
17	1.99	0.660	0.503
19	1.85	0.692	0.541
21	1.68	0.734	0.595

Between t = 9hrs. and t = 21hrs. 1 / p-x is linear with slope 0.0247.

This corresponds with $k_2 = 3.205 \times 10^{-8}$ moles.secs.$^{-1}$litres.$^{-1}$

Table 10 (a)[2]

a = b = 0.0425M pH = 7.40 Temperature = 35.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	1hr.	46mins.	61.87
0	5	96.25	2	26	53.42
0	10	92.92	3	29	42.96
0	20	86.74	4	27	37.84
0	31	83.04	5	27	33.08
0	48	75.91	6	36	28.44
1	11	70.55	7	56	24.99

Table 10 (b)[2]

a = b = 0.0425M pH = 7.40 Temperature = 35.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
Ohrs.	9.10mls.	0.000	0.110mls^{-1}
1/4	8.13	0.049	0.123
1/2	7.58	0.080	0.132
3/4	7.08	0.109	0.141
1	6.67	0.135	0.150
2	5.35	0.231	0.187
3	4.31	0.325	0.232
4	3.62	0.401	0.276
5	3.19	0.455	0.314
6	2.79	0.514	0.358
7	2.42	0.575	0.413

Between t = Ohrs. and t = 6hrs. 1 / p-x is linear with slope 0.0413.

This corresponds with $k_2 = 5.359 \times 10^{-8}$ moles.secs.$^{-1}$ litres.$^{-1}$

Table 11 (a)[2]

a = b = 0.0425M pH = 8.21 Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	9hrs.	36mins.	27.98
0	20	90.53	10	43	25.92
0	45	83.94	12	36	24.09
1	6	79.08	13	59	23.12
2	1	68.16	15	27	21.50
3	39	54.12	16	57	20.10
5	1	45.15	18	27	18.36
6	30	37.49	19	58	17.40
8	2	31.54	21	27	16.74

Table 11 (b)[2]

a = b = 0.0425M pH = 8.21 Temperature = 25.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
Ohrs.	7.96mls.	0.000	0.127mls.$^{-1}$
2	5.51	0.160	0.182
4	4.10	0.288	0.244
6	3.18	0.399	0.315
8	2.52	0.500	0.397
10	2.18	0.563	0.459
12	1.96	0.609	0.510
14	1.76	0.656	0.568
16	1.57	0.705	0.637
18	1.45	0.740	0.690
20	1.37	0.764	0.730

Between t = Ohrs. and t = 16hrs. 1 / p-x is linear with slope 0.0319.

This corresponds with $k_2 = 4.139 \times 10^{-8}$ moles.secs.$^{-1}$litres.$^{-1}$

Table 12 (a)[2]

a = b = 0.0425M pH = 8.21 Temperature = 35.0°C.

Time.	% $Na_2S_2O_3$ remaining.	Time.	% $Na_2S_2O_3$ remaining.
0hrs. 0mins.	100.00	1hr. 49mins.	57.03
0 7	94.15	2 21	50.87
0 18	87.54	2 44	46.42
0 29	81.49	3 17	41.45
0 44	75.75	4 15	34.95
0 59	71.20	5 4	31.49
1 17	66.77	5. 37	29.00
1 35	61.58	7 22	25.65

Table 12 (b)[2]

a = b = 0.0425M pH = 8.21 Temperature = 35.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
0hrs.	7.96mls.	0.000	0.127mls.$^{-1}$
1	5.61	0.152	0.178
2	4.33	0.264	0.231
3	3.49	0.359	0.287
4	2.91	0.437	0.344
5	2.48	0.507	0.403
6	2.24	0.551	0.446
7	2.09	0.581	0.479

Between t = 0hrs. and t = 6hrs. 1 / p-x is linear with slope 0.0532.

This corresponds with $k_2 = 6.903 \times 10^{-8}$ moles.secs.$^{-1}$ litres.$^{-1}$

Table 13 (a)[2]

a = b = 0.0425M pH = 8.31 Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	7hrs.	54mins.	37.24
0	22	89.75	9	56	31.11
0	42	85.19	12	32	27.03
1	14	78.86	14	0	25.85
2	2	72.31	15	39	24.68
3	44	57.26	19	18	21.32
5	43	46.15	21	30	20.52

Table 13 (b)[2]

a = b = 0.0425M pH = 8.31 Temperature = 25.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
Ohrs.	5.01mls.	0.000	0.200mls.$^{-1}$
1	4.10	0.087	0.244
2	3.57	0.147	0.280
4	2.79	0.254	0.358
6	2.22	0.353	0.451
8	1.81	0.442	0.553
10	1.58	0.501	0.633
12	1.39	0.556	0.719
14	1.27	0.596	0.787
16	1.18	0.628	0.848
18	1.10	0.658	0.909

Between t = Ohrs. and t = 12hrs. 1 / p-x is linear with slope 0.0433.

This corresponds with $k_2 = 5.618 \times 10^{-8}$ moles.secs.$^{-1}$litres.$^{-1}$

Table 14 (a)[2]

a = b = 0.0425M pH = 8.31 Temperature = 35.0°C.

Time.	% $Na_2S_2O_3$ remaining.	Time.	% $Na_2S_2O_3$ remaining.
0hrs. 0mins.	100.00	2hrs. 18mins.	52.49
0 11	92.49	3 9	44.76
0 21	88.13	4 8	37.23
0 37	81.00	5 5	32.67
0 54	74.67	6 5	29.51
1 15	68.13	7 7	28.13
1 47	59.80	8 3	25.55

Table 14 (b)[2]

a = b = 0.0425M pH = 8.31 Temperature = 35.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
0hrs.	5.01mls.	0.000	0.200mls.$^{-1}$
1	3.60	0.143	0.278
2	2.80	0.252	0.357
3	2.28	0.341	0.439
4	1.93	0.414	0.518
5	1.70	0.469	0.588
6	1.54	0.512	0.649
7	1.42	0.547	0.704
8	1.29	0.589	0.775

Between t = 0hrs. and t = 5hrs. 1 / p-x is linear with slope 0.0776.

This corresponds with $k_2 = 10.065 \times 10^{-8}$ moles.secs.$^{-1}$ litres.$^{-1}$

Table 15 (a)[2]

a = b = 0.0425M pH = 8.62 Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	9hrs.	36mins.	31.12
0	20	90.65	10	35	29.05
0	40	86.95	12	40	26.88
1	1	83.68	13	54	25.36
2	2	73.34	15	35	23.62
3	28	61.70	17	9	22.09
5	1	49.95	18	26	20.68
6	32	41.35	20	10	20.57
7	58	36.01	21	47	20.02

Table 15 (b)[2]

a = b = 0.0425M pH = 8.62 Temperature = 25.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
0hrs.	7.62mls.	0.000	0.131mls.$^{-1}$
2	5.66	0.129	0.177
4	4.36	0.243	0.229
6	3.37	0.354	0.297
8	2.72	0.448	0.368
10	2.34	0.513	0.427
12	2.11	0.558	0.474
14	1.90	0.603	0.526
16	1.75	0.639	0.571
18	1.63	0.670	0.614
20	1.58	0.683	0.633

Between t = 0hrs. and t = 16hrs. 1 / p-x is linear with slope 0.0280.

This corresponds with $k_2 = 3.633 \times 10^{-8}$ moles.secs.$^{-1}$ litres.$^{-1}$

Table 16 (a)[2]

a = b = 0.0425M pH = 8.62 Temperature = 35.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
0hrs.	0mins.	100.00	2hrs.	10mins.	57.72
0	6	95.81	2	49	50.09
0	19	89.80	3	21	43.54
0	30	85.23	4	22	38.84
0	51	78.89	5	35	33.60
1	3	75.40	6	21	31.10
1	35	66.67	7	45	28.70

Table 16 (b)[2]

a = b = 0.0425M pH = 8.62 Temperature = 35.0°C.

Time.	(p-x)	$\log_{10}$ p/ p-x	1 / p-x
0hrs.	7.62mls.	0.000	0.131mls.$^{-1}$
1	5.81	0.118	0.172
2	4.59	0.220	0.218
3	3.68	0.316	0.272
4	3.08	0.394	0.325
5	2.71	0.449	0.369
6	2.46	0.491	0.407
7	2.29	0.522	0.437

Between t = 0hrs. and t = 5hrs. 1 / p-x is linear with slope 0.0472.

This corresponds with $k_2 = 6.123 \times 10^{-8}$ moles.secs.$^{-1}$ litres.$^{-1}$

Table 17 (a)[2]

a = b = 0.0425M pH = 8.97 Temperature = 25.0°C.

Time.	% $Na_2S_2O_3$ remaining.	Time.	% $Na_2S_2O_3$ remaining.
0hrs.0mins.	100.00	10hrs.58mins.	36.76
0 20	92.19	12 29	34.60
0 42	89.83	13 54	32.83
0 59	86.98	15 26	30.07
2 5	82.57	16 52	28.41
3 40	72.04	18 25	26.64
5 6	63.01	19 57	26.15
6 39	53.96	21 28	25.66
8 5	47.66	22 56	25.07
9 32	41.18		

Table 17 (b)[2]

a = b = 0.0425M pH = 8.97 Temperature = 25.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
0hrs.	6.95mls.	0.000	0.144mls.$^{-1}$
2	5.54	0.099	0.181
4	4.74	0.167	0.211
6	3.98	0.242	0.251
8	3.61	0.285	0.277
10	2.81	0.394	0.356
12	2.43	0.457	0.412
14	2.18	0.504	0.459
16	1.98	0.546	0.505
18	1.87	0.570	0.535
20	1.79	0.589	0.559

Between t = 0hrs. and t = 16hrs. 1 / p-x is linear with slope 0.0226.

This corresponds with $k_2 = 2.927 \times 10^{-8}$ moles.secs.$^{-1}$ litres.$^{-1}$

Table 18 (a)[2]

a = b = 0.0425M pH = 8.97 Temperature = 35.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	3hrs.	Omins.	52.84
0	7	91.93	3	30	47.84
0	15	88.98	4	1	44.10
0	26	83.78	4	34	42.33
0	38	80.82	5	33	38.20
0	53	78.18	6	34	34.76
1	12	74.05	7	33	32.50
2	3	62.56	8	32	31.63
2	34	57.07			

Table 18 (b)[2]

a = b = 0.0425M pH = 8.97 Temperature = 35.0°C.

Time.	(p-x)	$\log_{10}$ p/ p-x	1 / p-x
Ohrs.	6.95mls.	0.000	0.144mls.$^{-1}$
1	5.25	0.122	0.191
2	4.34	0.205	0.230
3	3.66	0.279	0.273
4	3.12	0.348	0.321
5	2.78	0.398	0.360
6	2.51	0.443	0.398
7	2.33	0.475	0.429
8	2.24	0.492	0.446

Between t = Ohrs. and t = 6hrs. 1 / p-x is linear with slope 0.0423.

This corresponds with $k_2 = 5.487 \times 10^{-8}$ moles.secs.$^{-1}$ litres.$^{-1}$

Table 19 (a)[2]

a = b = 0.0425M pH = 8.98 Temperature = 25.0°C.

Time.	% $Na_2S_2O_3$ remaining.	Time.	% $Na_2S_2O_3$ remaining.
0hrs. 0mins.	100.00	10hrs. 53mins.	34.53
0 20	91.70	12 19	33.61
0 42	88.88	13 49	30.94
1 2	85.70	15 12	29.01
2 1	78.97	16 42	27.48
3 28	68.73	18 18	25.74
5 1	58.74	19 40	24.62
6 30	49.94	21 10	24.71
8 1	41.98	22 40	23.90
9 30	37.99		

Table 19 (b)[2]

a = b = 0.0425M pH = 8.98 Temperature = 25.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
0hrs.	6.95mls.	0.000	0.144mls.$^{-1}$
2	5.48	0.104	0.183
4	4.51	0.188	0.222
6	3.59	0.287	0.279
8	2.94	0.374	0.340
10	2.56	0.434	0.391
12	2.28	0.484	0.439
14	2.08	0.524	0.481
16	1.91	0.561	0.524
18	1.80	0.587	0.556
20	1.74	0.602	0.575

Between t = 0hrs. and t = 16hrs. 1 / p-x is linear with slope 0.0238.

This corresponds with $k_2 = 3.081 \times 10^{-8}$ moles.secs.$^{-1}$litres.$^{-1}$

Table 20 (a)[2]

a = b = 0.0425M pH = 8.98 Temperature = 35.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	3hrs.	Omins.	57.08
0	8	94.20	3	31	51.98
0	19	90.76	4	0	48.43
0	30	87.20	4	36	45.88
0	41	85.55	5	19	42.63
0	56	81.40	5	58	40.20
1	15	77.43	6	50	36.83
1	43	71.73	7	34	36.12
2	9	66.04	8	20	27.48
2	30	61.64			

Table 20 (b)[2]

a = b = 0.0425M pH = 8.98 Temperature = 35.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
Ohrs.	6.95mls.	0.000	0.144mls.$^{-1}$
1	5.60	0.094	0.179
2	4.68	0.172	0.214
3	3.99	0.241	0.251
4	3.46	0.303	0.289
5	3.07	0.355	0.326
6	2.78	0.398	0.360
7	2.58	0.431	0.388
8	2.45	0.453	0.408

Between t = Ohrs. and t = 6hrs. 1 / p-x is linear with slope 0.0360.

This corresponds with $k_2 = 4.671 \times 10^{-8}$ moles.secs.$^{-1}$litres.$^{-1}$

Table 21 (a)[2]

a = b = 0.0425M pH = 9.00 Temperature = 25.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	7hrs.	52mins.	50.12
0	24	92.96	9	54	44.79
0	43	89.18	12	28	39.63
1	15	86.63	13	56	37.64
2	2	80.93	15	36	36.27
3	46	68.68	19	16	35.06
5	41	60.57	21	26	33.49

Table 21 (b)[2]

a = b = 0.0425M pH = 9.00 Temperature = 25.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
Ohrs.	5.01mls.	0.000	0.200
2	3.99	0.098	0.251
4	3.33	0.177	0.300
6	2.88	0.240	0.347
8	2.50	0.301	0.400
10	2.24	0.349	0.446
12	2.05	0.388	0.488
14	1.92	0.416	0.521
16	1.84	0.435	0.544
18	1.77	0.451	0.565

Between t = Ohrs. and t = 10hrs. 1 / p-x is linear with slope 0.0246.

This corresponds with $k_2 = 3.191 \times 10^{-8}$ moles.secs.$^{-1}$litres.$^{-1}$

Table 22 (a)[2]

a = b = 0.0425M pH = 9.00 Temperature = 35.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	2hrs.	15mins.	72.10
0	7	95.06	3	6	63.79
0	17	91.70	4	3	55.64
0	32	87.34	5	2	51.89
0	51	84.95	6	12	47.94
1	12	80.80	7	4	45.35
1	44	75.83	8	0	43.38

Table 22 (b)[2]

a = b = 0.0425M pH = 9.00 Temperature = 35.0°C.

Time.	(p-x)	$\log_{10}$ p / p-x	1 / p-x
Ohrs.	5.01mls.	0.000	0.200mls.$^{-1}$
1	4.11	0.086	0.243
2	3.61	0.142	0.277
3	3.20	0.194	0.313
4	2.83	0.248	0.353
5	2.59	0.286	0.386
6	2.40	0.319	0.417
7	2.25	0.347	0.444
8	2.15	0.367	0.465

Between t = Ohrs. and t = 5hrs. 1 / p-x is linear with slope 0.0372.

This corresponds with $k_2 = 4.827 \times 10^{-8}$ moles.secs.$^{-1}$litres.$^{-1}$

Table 23.(2)

a = b = 0.0425M pH = 11.2 Temperature = 35.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	14hrs.	32mins.	61.58
1	21	99.34	16	0	50.10
4	25	96.20	17	25	41.67
6	39	95.58	18	54	33.11
8	43	94.10	19	56	27.40
11	1	91.56	22	33	24.93
13	8	76.55			

An induction period of about eleven hours was observed under these conditions.

REACTION IN MIXTURE BUFFERED TO pH 5·53.

c.f. Table 1a[2].

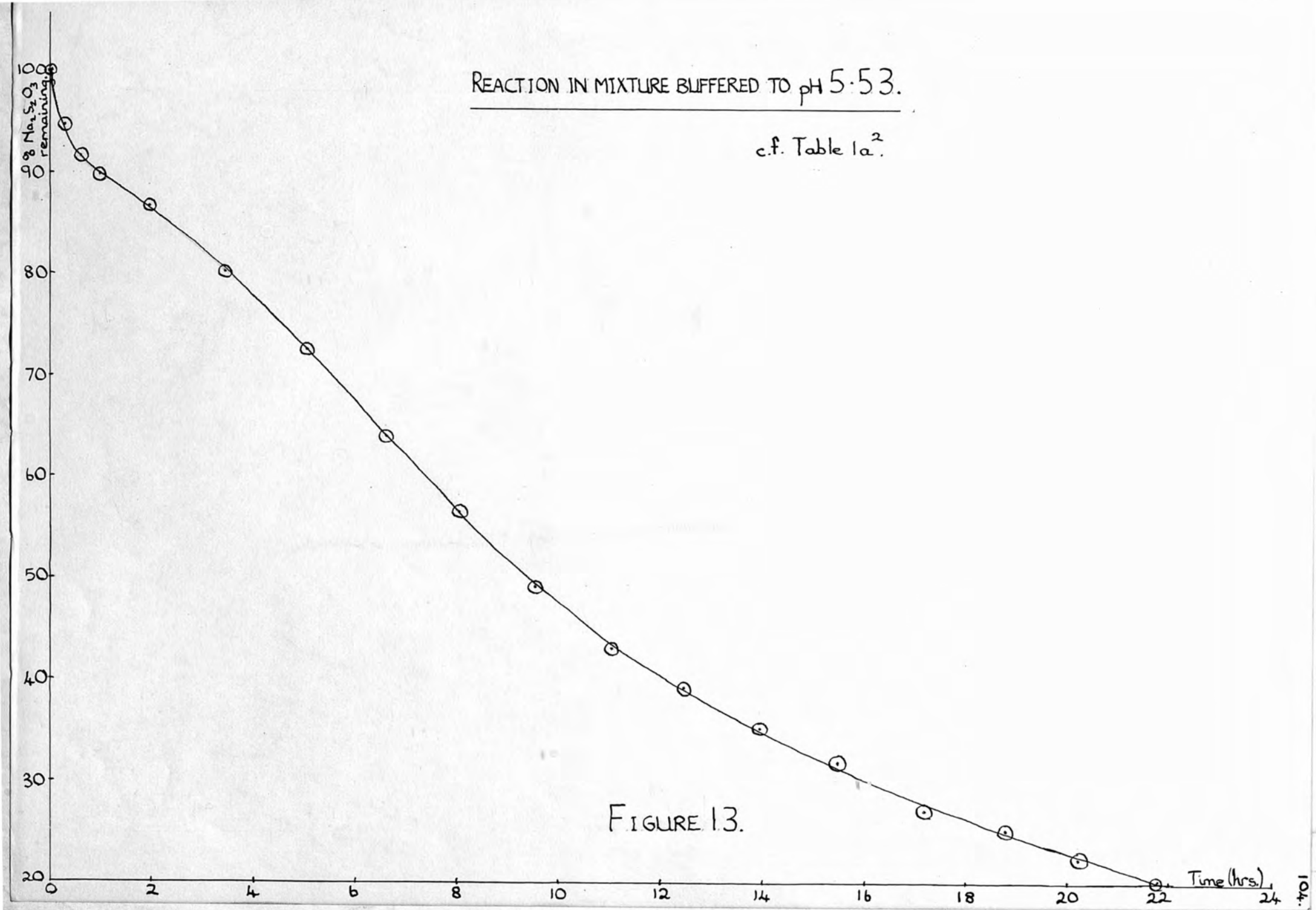


FIGURE 13.

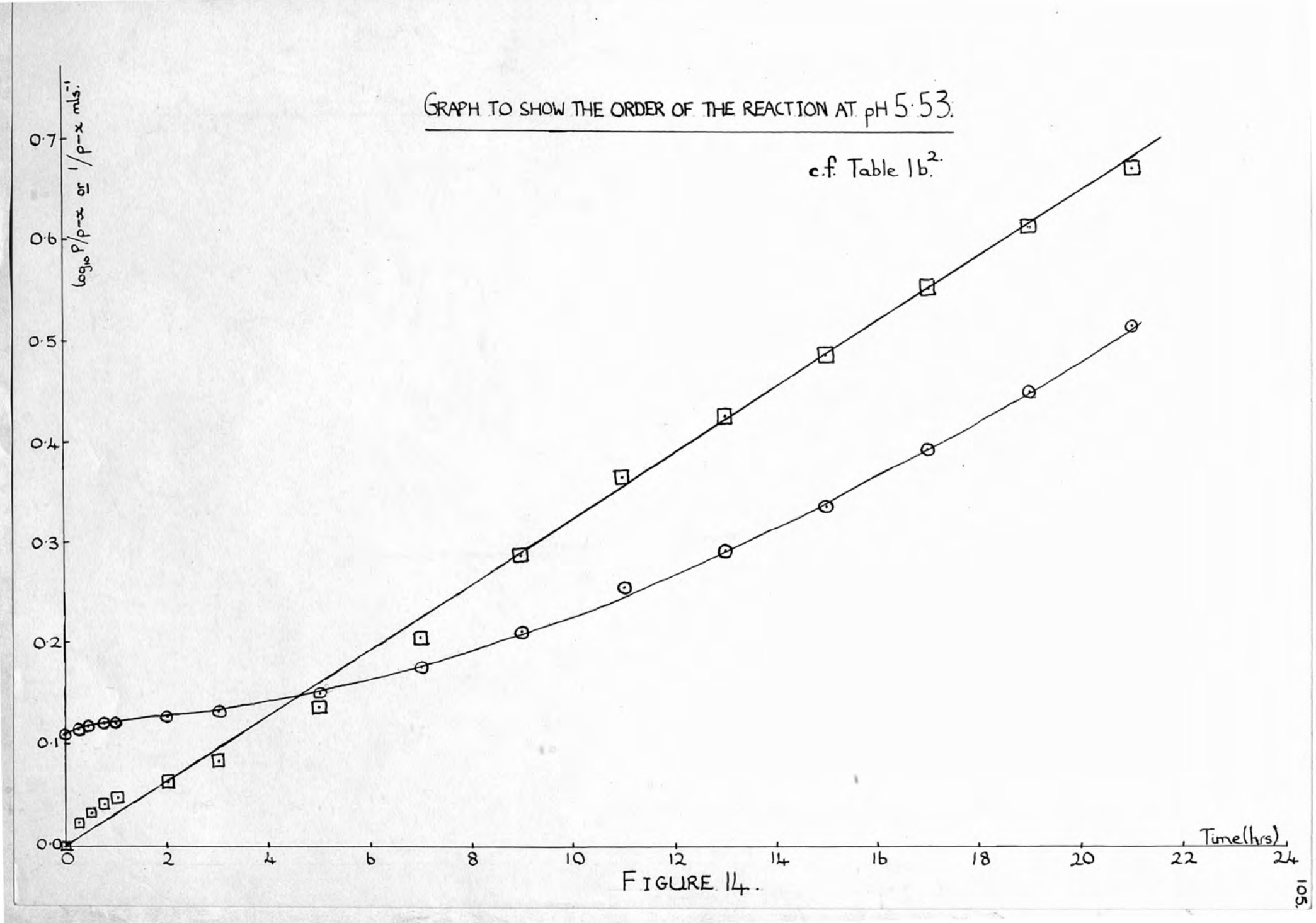

GRAPH TO SHOW THE ORDER OF THE REACTION AT pH 5·53.
c.f. Table 1b.2.
log10 P/p-x or 1/p-x mls-1
0·0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0
2
4
6
8
10
12
14
16
18
20
22
24
Time (hrs)

FIGURE 14.

REACTION IN MIXTURE BUFFERED TO pH 9·00.

c.f. Table 22a².

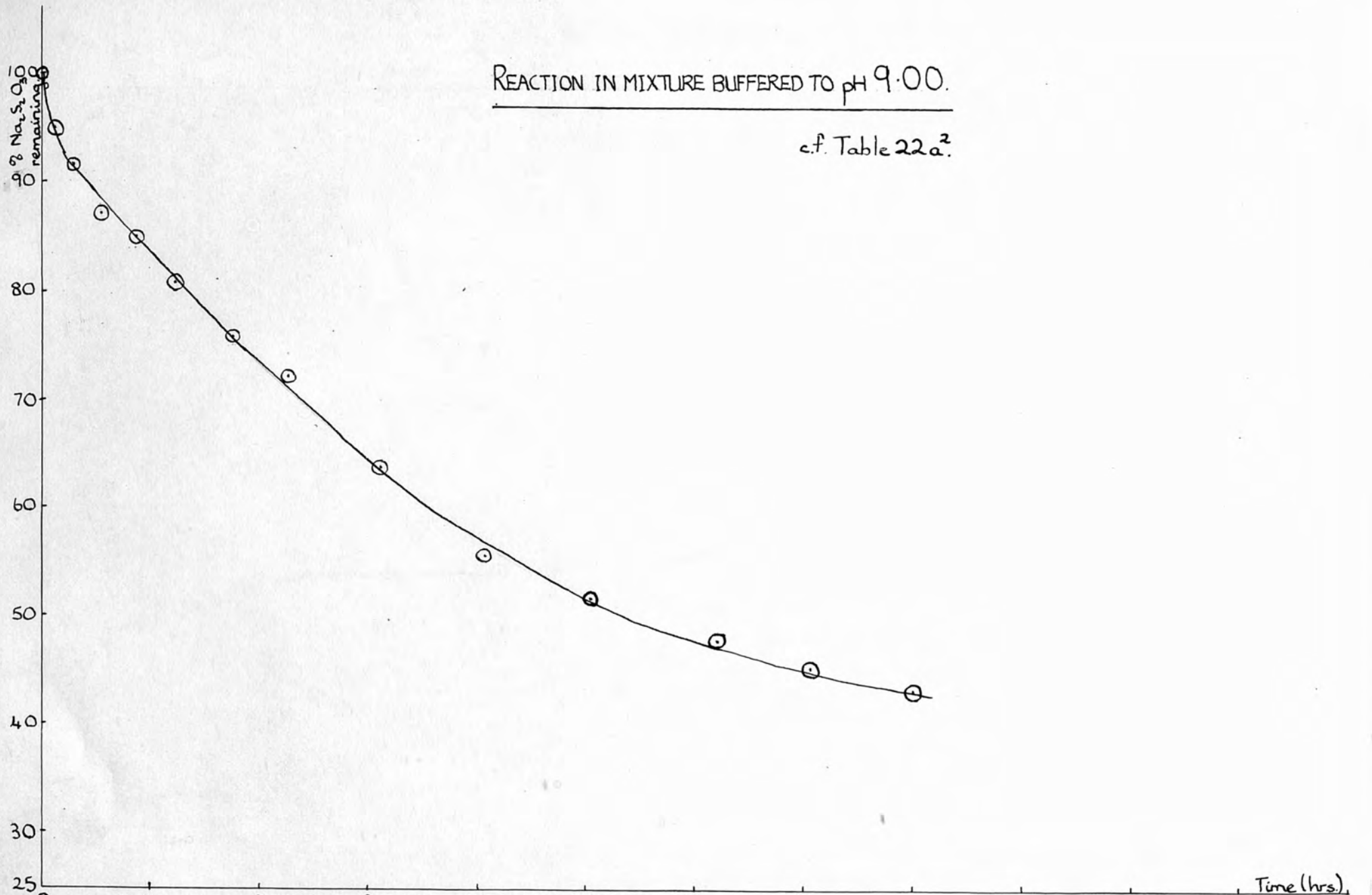


FIGURE 15.

GRAPH TO SHOW THE ORDER OF THE REACTION AT pH 9·00.

c.f. Table 22b[2].

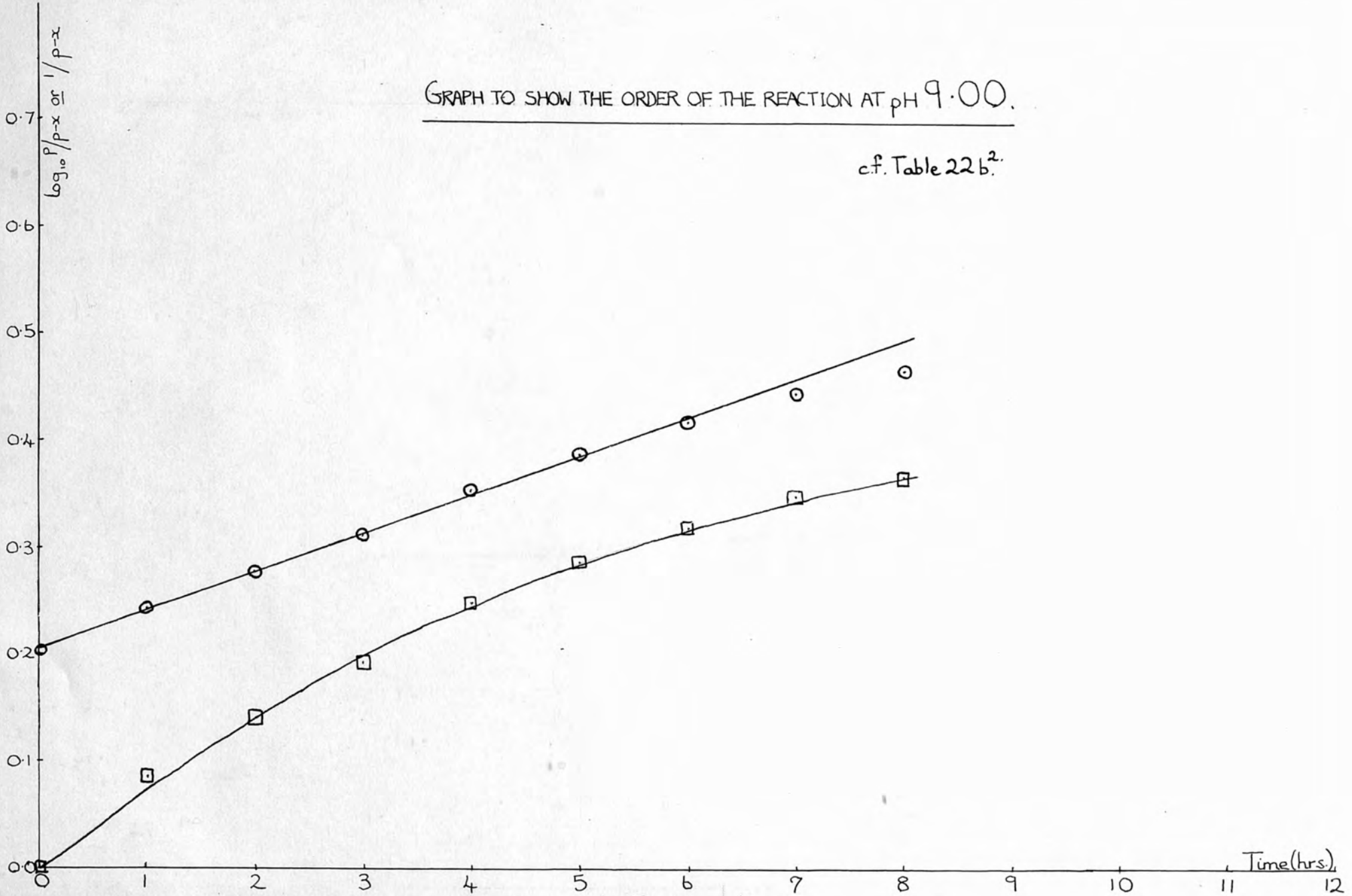


FIGURE 16.

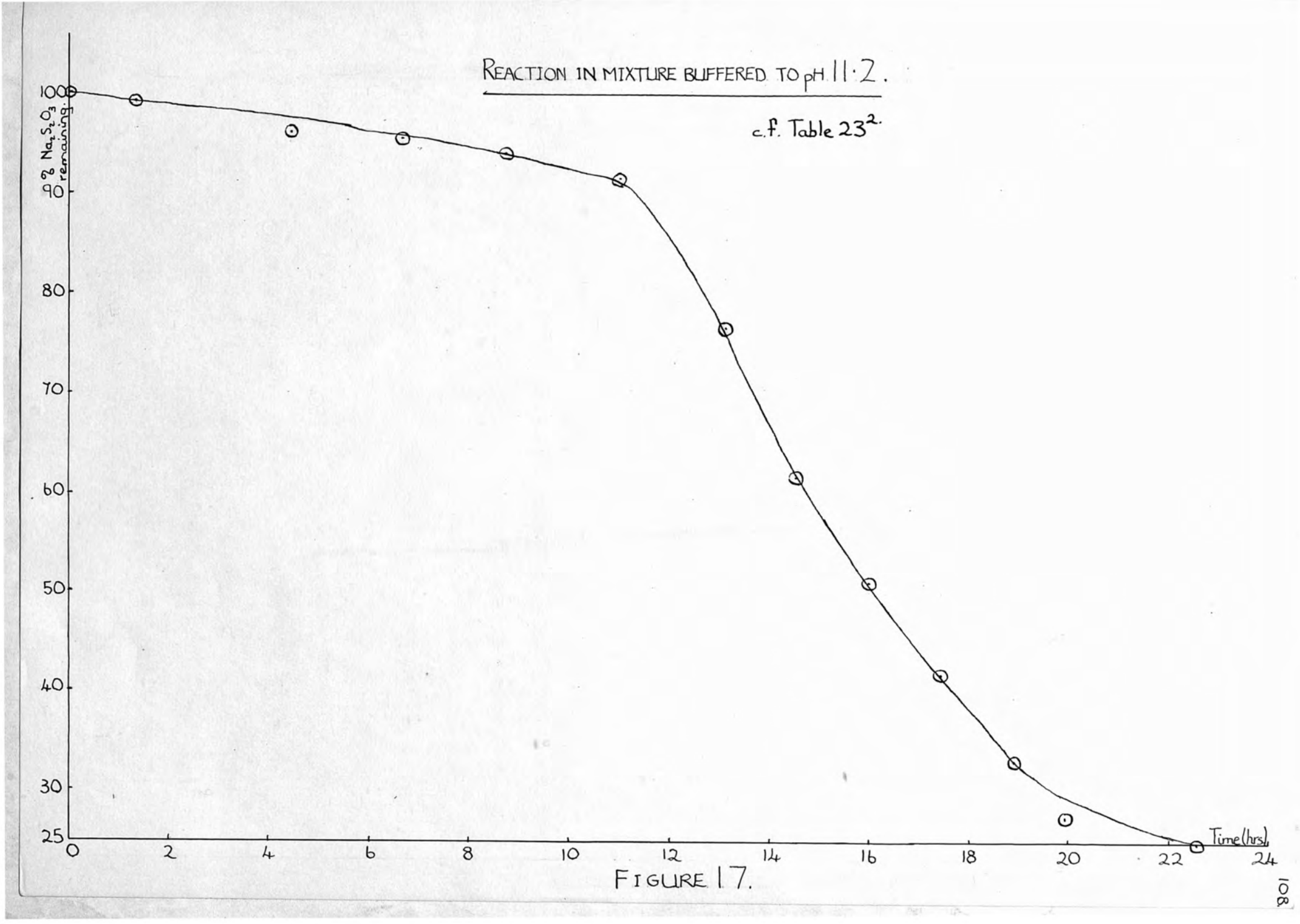

REACTION IN MIXTURE BUFFERED TO pH 11·2.
c.f. Table 23².
% $Na_2S_2O_3$ remaining.
100
90
80
70
60
50
40
30
25
0
2
4
6
8
10
12
14
16
18
20
22
24
Time (hrs).

FIGURE 17.

Section 2.

The products of the reaction.

(1) Experiments to confirm the nature of the products.

Sandved and Holte[12] seem to have established the fact that the reaction under consideration does follow the stoichiometric equation

$$2\ Fe(CN)_6^{'''} + 2\ S_2O_3^{''} = 2\ Fe(CN)_6^{''''} + S_4O_6^{''} \quad (6)$$

It was decided to make a further check on this result in view of the importance of having a certain knowledge of the products of the reaction before attempting to elucidate its kinetics.

Assuming that equation (6) is obeyed, it is possible to calculate the amounts of the reactants and products present in the reacting mixture at any given stage of the reaction. This calculation was made for reactions occurring with various initial concentrations of sodium thiosulphate and potassium ferricyanide. Mixtures were then prepared containing these proportions of sodium thiosulphate, potassium ferricyanide, potassium ferrocyanide and sodium tetrathionate, and they were allowed to react under the same conditions as in the previous experiments with comparable conditions.

The results obtained would be expected to fit on to the corresponding reaction curve for an initial mixture of

sodium thiosulphate and potassium ferricyanide only. It can be seen from the results shown in Tables $24^{(2)}$ and $25^{(2)}$ and in Fig.18, that within the limits of experimental error, this does occur.

The preparation of the sodium tetrathionate used in these experiments is descibed in Appendix 2.

Certain of the above experiments were carried out by preparing inital mixtures of sodium thiosulphate and potassium ferricyanide and comparing the reaction curve obtained in these cases with one obtained from a mixture made to correspond with the expected state after a given percentage reaction, but less the sodium tetrathionate.

The comparable curves obtained in this way were also superimposable, within the limits of experimental accuracy. This result seems to indicate that the sodium tetrathionate concentration has relatively little effect upon the rate of the reaction in the later stages, although in mixtures shielded from light there is a slight indication of a more rapid reaction in the presence of tetrathionate. At the same time this result does not coincide with the observation of Sandved and Holte, who found that omission of the sodium tetrathionate caused a considerable decrease in the rate of the reaction. A difference between the two sets of experiments, however, was that in the present work the mixtures used corresponded to two-thirds complete

reaction between the ferricyanide and thiosulphate, whereas Sandved and Holte's mixtures corresponded with a much smaller percentage reaction. These two results taken together, therefore, are in agreement with the conclusion drawn from experiments described in Section 3 of this chapter, that the effect of sodium tetrathionate is greater in the earlier stages than in the later stages of the reaction.

The composition of mixtures (a),(b),and (c), used in the experiments, the results of which are shown in Tables 24 and 25 were as follows:-

(a) 0.0425M in potassium ferricyanide and sodium thiosulphate.

(b) 0.0142M in potassium ferricyanide, sodium thiosulphate and sodium tetrathionate. 0.0283M in potassium ferrocyanide.

(c) 0.0142M in potassium ferricyanide and sodium thiosulphate. 0.0283M in potassium ferrocyanide.

Table 24.(2)

pH = 7.40 Temperature = 35.0°C.

Time.	% $Na_2S_2O_3$ remaining.		
	Mixture (a)	Mixture (b)	Mixture (c)
0hrs. 0mins.	100.00	100.00	100.00
0 6	95.42		
0 13	91.52		
0 27	84.21		
0 43	77.75		
1 6	70.08		
2 5	53.75		
2 37	48.63		
3 9	43.75		
3 49	39.85		
4 53	36.32		
5 46		33.14	
5 54			33.52
6 28	31.20		
7 14			28.03
7 16		28.27	
8 26	26.08		
8 35		25.59	
8 41			24.86
10 7			23.03
10 22		23.03	
10 36	22.05		
11 46			21.09
12 19	18.29		
13 19			19.37
13 41		18.65	
14 18	14.26		
14 44			17.79
15 17		16.95	
15 58	9.04		
16 12			16.69

In Tables 24 and 25 the % $Na_2S_2O_3$ remaining is calculated as though the mixtures were originally 0.0425M in this compound. The reaction with mixtures (b) and (c) actually commenced at 5hrs. 41mins.

Table 25.(2)

pH = 8.21 Temperature = 35.0°C.

Time.	% reaction.		
	Mixture (a)	Mixture (b)	Mixture (c)
0hrs. 0mins.	100.00	100.00	100.00
0 7	94.42		
0 17	89.35		
0 31	83.38		
1 0	71.97		
1 46	60.02		
2 47	46.90		
3 43	39.37		
4 55			28.82
4 59		29.26	
5 50	30.23		
6 33			23.39
6 36		24.34	
7 36	25.53		
8 45			20.62
8 47	23.17		
8 49		19.59	
10 31	21.16		18.48
10 35		18.30	
12 29			17.09
12 34		16.57	
12 50	19.83		
14 26			15.62
14 28		15.80	
15 17	17.21		
17 36	14.31		

This reaction was carried out in foil covered bottles.

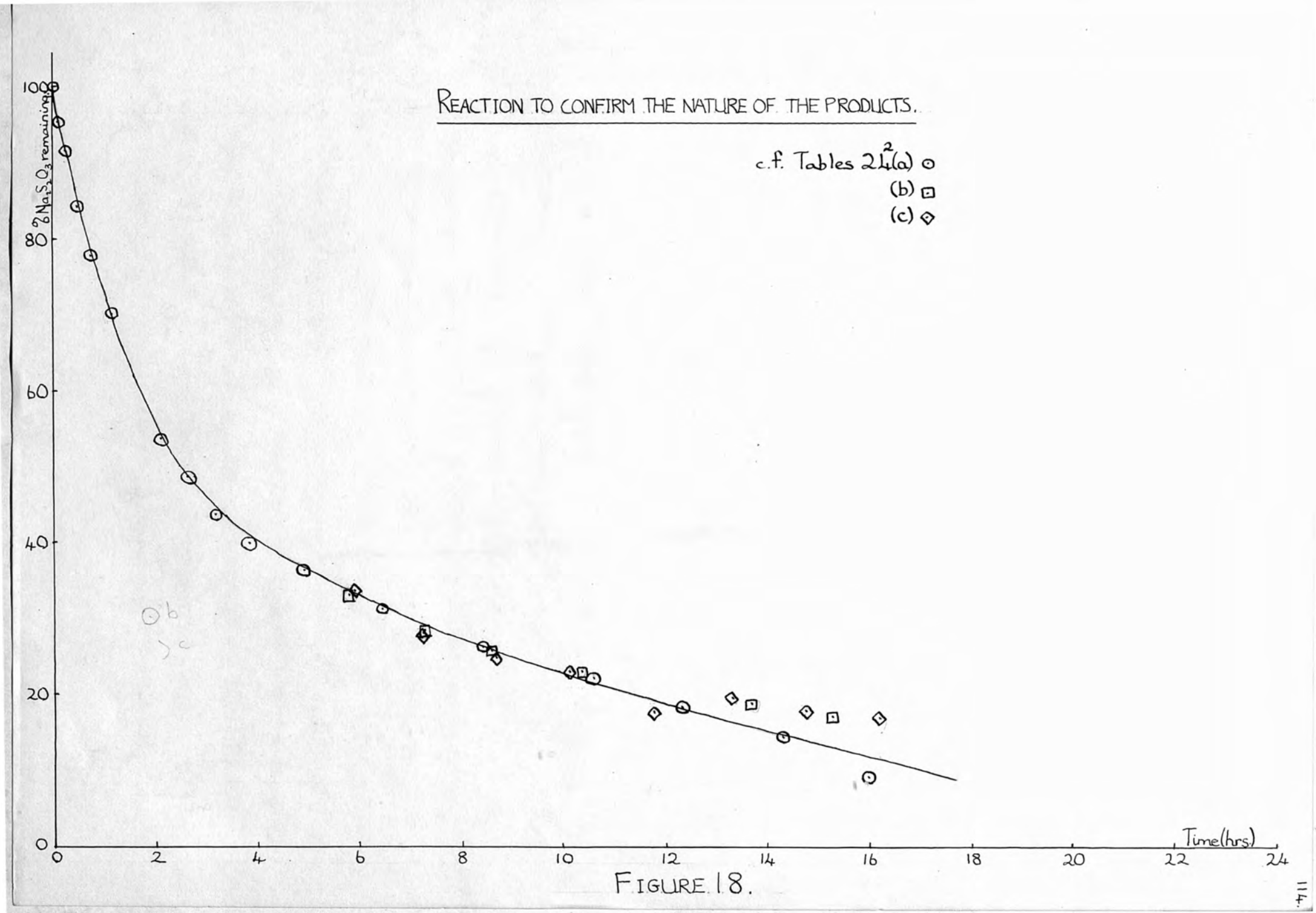


FIGURE 18.

F.11

(2) The effect of ferrocyanide ions on the reaction.

Preliminary experiments had shown that potassium ferrocyanide had a considerable retarding effect on the reaction between potassium ferricyanide and sodium thiosulphate. The experiments recorded in Chapter 1. Section 2.8 have only demonstrated this effect qualitatively; the work described in this section is an attempt to investigate it quantitatively.

The kinetic runs were all carried out in solutions buffered to pH 7.40, as under such conditions the reaction seemed to show a minimum of abnormalities. Mixtures of sodium thiosulphate and potassium ferricyanide, with varying amounts of potassium ferrocyanide were prepared. The course of the reaction was followed in the usual way.

As the initial concentration of potassium ferrocyanide was increased from zero to 0.128M the retarding effect observed increased to a maximum and then began to decrease. It seems likely that this was due to the direct retarding effect of the ferrocyanide being opposed by a positive primary salt effect produced by the considerable increase in ionic strength on addition of the quadrivalent ion.

A parallel series of experiments was carried out using mixtures of potassium ferricyanide and sodium thiosulphate solutions to which standard potassium chloride solution was added. By this means, the ionic strengths of the mixtures

could be varied so that they were equivalent to the initial values of this quantity in the experiments where potassium ferrocyanide was added.

When the results obtained under these conditions were compared, the retarding effect of the ferrocyanide ion became more clearly apparent. Some of these results are given in Tables 26^2, 28^2, 30^2, 32^2, 33^2, 34^2 and 35^2 and also in Fig. 19.

The retardation effect is considerable in the early stages of the reaction but later it is no longer noticeable, and the reaction curves obtained under similar conditions of temperature, concentration and ionic strength from these two series of experiments, become superimposable.

The amount of potassium ferrocyanide used in the majority of these experiments was small, and the retardation produced by it was approximately proportional to its concentration. When larger quantities of this ion were present, however, the proportionality between concentration and retardation no longer held.

Sandved and Holte [5] had very different findings regarding the effect of additions of potassium ferrocyanide. They inferred that in buffered solutions containing this substance, as well as potassium ferricyanide and sodium thiosulphate, the potassium ferrocyanide serves merely to eliminate the peculiarities observed at the beginning of the reaction. No additional retardation was observed. The

retarding effect observed in the present work however, was considerable, but was most noticeable in the early stages of the reaction: it seems most likely that, since they worked with solutions of very high ionic strength, the reaction proceeded very rapidly and hence the full effects of these additions on the early stages of the reaction were unnoticed.

This retardation by ferrocyanide ions tends to suggest that they participate in a reversible process which is a vital step in the reaction mechanism.

(3) The effect of tetrathionate ions on the reaction.

Sodium tetrathionate has also been shown to have an effect on the rate of the reaction between sodium thiosulphate and potassium ferricyanide. Again, qualitative experiments have been described in Chapter 1 Section 2.9 which illustrate this. As in the case of potassium ferrocyanide, a further series of quantitative experiments have been carried out to investigate the effect in greater detail.

All the kinetic runs were carried out in solution mixtures buffered to a pH value of 7.40 in order to avoid unnecessary complications. Mixtures of sodium thiosulphate and potassium ferricyanide solutions were prepared and the ionic strengths of the mixtures were brought up to certain fixed values by the addition of either standard sodium

tetrathionate solution or standard potassium chloride solution.*

A comparison between these two sets of experiments showed that when small quantities of sodium tetrathionate were added the reaction rate was speeded up approximately in proportion to the amount added. When larger quantities of this ion were used the acceleration produced seemed to increase to a maximum. These results suggest that if the concentration of sodium tetrathionate in the initial mixture was increased considerably, there would be very little further increase in the speed of the reaction.

The preparation of solutions of sodium tetrathionate of higher concentration than those used here was attempted, with a view to testing this hypothesis but difficulties arose owing to the deposition of sulphur under these conditions. This difficulty has not been overcome.

* Some of these results are given in Tables 27, 28, 29, 30, 31, and in Fig. 19.

THE EFFECT OF THE PRODUCTS ON THE REACTION RATE.

FIGURE 19.

c.f. Tables 28^2 (a) ⊙
(b) ◇
(c) ⊡

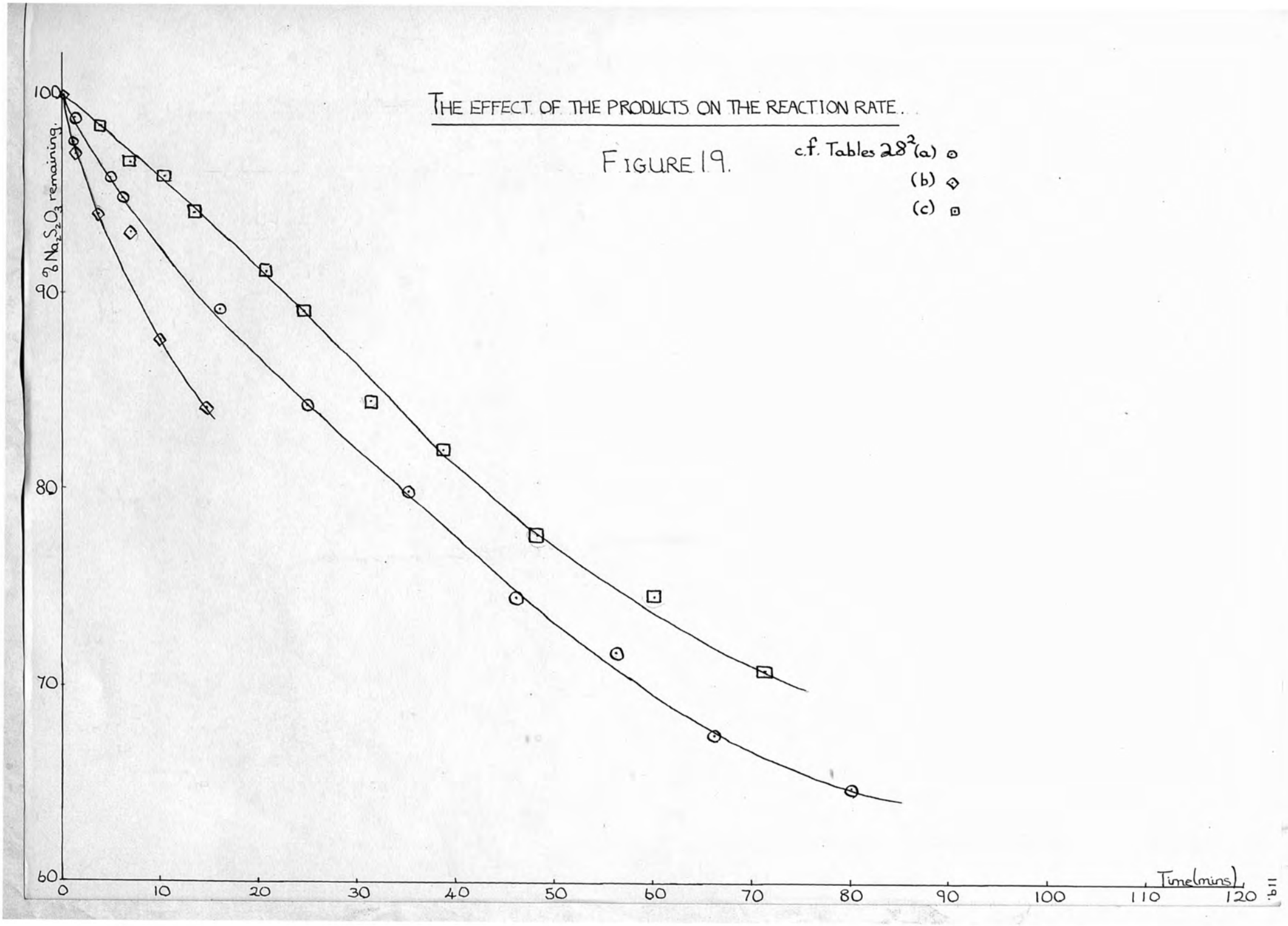


Table 26.(2)

a = b = 0.0425M pH = 7.40 μ = 1.83 Temperature = 35.0°C.

Time.		% $Na_2S_2O_3$ remaining.	Time.		% $Na_2S_2O_3$ remaining.
Ohrs.	Omins.	100.00	Ohrs.	13.0mins.	90.26
0	1.5	97.66	0	18.0	87.22
0	3.5	96.62	0	38.5	78.05
0	4.5	96.33	0	48.5	73.47
0	6.0	94.15	1	0.5	71.47
0	7.0	93.48	1	10.5	68.22
0	9.5	92.82	1	20.0	65.84
0	11.0	91.78			

μ = Ionic strength.

Table 27.[2]

a = b = 0.0425M pH = 7.40 μ = 1.84 Temperature = 35.0°C

Time.		% $Na_2S_2O_3$ remaining.	
		Mixture (a)[1]	Mixture (b)[1]
0mins.	0secs.	100.00	100.00
1	26	98.11	
1	33		96.58
2	54		94.49
4	39		93.35
5	24	95.96	
7	27		90.03
10	10		87.94
12	22	91.49	
13	6		84.71
15	10		84.33
16	15	89.44	
17	48		81.48
20	1		80.73
25	47	84.32	

Mixture (a)[1] is 0.01M in KCl.

Mixture (b)[1] is 0.0043M in $Na_2S_4O_6$.

Table 28.[2]

$a = b = 0.0425M$ pH = 7.40 $\mu = 1.85$ Temperature = 35.0°C

Time.		% $Na_2S_2O_3$ remaining.		
		Mixture (a)[2]	Mixture (b)[2]	Mixture (c)[1]
0mins.	0secs.	100.00	100.00	100.00
1	12	98.71		
1	22		96.78	98.85
3	43		94.02	
3	55			98.57
4	49	95.88		
6	8	94.94		
6	27		93.13	
6	51			96.72
9	56		87.56	
10	23			95.97
13	32			94.10
14	35		84.24	
15	58	89.09		
20	47			91.13
24	32			89.08
24	58	84.33		
31	12			85.45
35	12	79.78		
38	48			82.01
46	10	74.45		
48	11			77.73
56	19	71.74		
60	4			74.47
66	15	67.36		
71	20			70.74
80	4	64.75		

Mixture (a)[2] is 0.02M in KCl.

Mixture (b)[2] is 0.0064M in $Na_2S_4O_6$.

Mixture (c)[1] is 0.0021M in $K_4Fe(CN)_6$.

Table 29.(2)

a = b = 0.0425M pH = 7.40 μ = 1.86 Temperature = 35.0°C

Time.		% $Na_2S_2O_3$ remaining.	
		Mixture $(a)^3$	Mixture $(b)^3$
Omins.	Osecs.	100.00	100.00
1	14	97.73	
1	34		95.64
1	55		95.15
2	7		95.54
4	9	96.05	
4	26		91.47
5	30		91.09
6	42		88.48
7	23		86.73
9	57		83.89
11	33		82.87
15	12		80.31
16	9	89.26	
18	13		77.36
20	18		75.55
24	50	83.94	
36	42	79.29	
45	31	74.16	

Mixture $(a)^3$ is 0.03M in KCl.

Mixture $(b)^3$ is 0.0085M in $Na_2S_4O_6$.

Table 30.(2)

a = b = 0.0425M pH = 7.40 μ = 1.87 Temperature = 35.0°C

Time.		% $Na_2S_2O_3$ remaining.		
		Mixture (a)^4	Mixture (b)^4	Mixture (c)^2
0mins.	0secs.	100.00	100.00	100.00
1	13		96.09	
1	27	97.39		
1	31		95.34	
2	43			99.87
2	44		93.24	
3	39	95.34		
4	33		91.15	
5	50		89.25	
6	12			97.64
7	25		86.59	
9	44			97.23
10	44		83.45	
12	13		81.54	
12	26	87.69		
13	55		80.02	
15	18			94.50
15	21		79.35	
16	14	85.54		
18	10		76.59	
19	10		76.40	
24	27			90.85
25	44	80.14		
28	23			89.13
31	56			87.71
34	56	75.46		
39	7			83.56
45	23			81.33
45	55	70.62		
50	48			79.30
55	8	67.17		
59	58			75.86
66	4	64.37		
70	18			72.72
80	8	59.61		69.69

Mixture (a)^4 is 0.04M in KCl.

Mixture (b)^4 is 0.0128M in $Na_2S_4O_6$.

Mixture (c)^2 is 0.0043M in $K_4Fe(CN)_6$.

Table 31.(2)

a = b = 0.0425M pH = 7.40 μ = 1.88 Temperature = 35.0°C

Time.		% $Na_2S_2O_3$ remaining.	
		Mixture (a)[5]	Mixture (b)[5]
0mins.	0secs.	100.00	100.00
1	30	97.05	
1	33		95.72
2	57		93.83
3	51		92.30
4	12	95.45	
5	27		89.08
6	38		87.46
7	40	92.31	
8	45		86.23
11	27		82.81
13	14		81.87
16	35		79.77
17	22	86.61	
19	4		77.30
25	16	81.48	
35	36	76.73	
44	59	71.60	
55	29	68.56	

Mixture (a)[5] is 0.05M in KCl.

Mixture (b)[5] is 0.017M in $Na_2S_4O_6$.

Table 32.[2]

a = b = 0.0425M pH = 7.40 μ = 1.92 Temperature = 35.0°C

Time.		% $Na_2S_2O_3$ remaining.	
		Mixture (a)[6]	Mixture (c)[3]
0mins.	0secs.	100.00	100.00
1	29	96.26	
4	19	93.01	
10	1		97.43
12	4	86.53	
15	48	84.24	96.22
21	32		92.27
25	48	77.75	
26	7		90.85
29	11		89.13
35	58	73.55	
40	10		84.47
45	58	68.02	
50	0		80.02
55	57	65.06	
58	47		77.27
66	12	60.48	
70	23		73.13
79	52	58.19	
81	13		70.69

Mixture (a)[6] is 0.09M in KCl.

Mixture (c)[3] is 0.0085M in $K_4Fe(CN)_6$.

Table 33.(2)

a = b = 0.0425M pH = 7.40 μ = 1.96 Temperature = 35.0°C

Time.		% $Na_2S_2O_3$ remaining.	
		Mixture $(a)^7$	Mixture $(c)^4$
Omins.	Osecs.	100.00	100.00
1	31	95.40	
3	36	93.88	
11	38		97.33
12	19	85.28	
15	58	81.57	
17	22		94.29
21	38		93.08
25	48	75.46	
27	41		89.84
30	49		88.52
35	55	71.16	
41	51		84.57
46	28	65.64	
50	35		80.02
60	53		77.48
65	47	58.86	
72	17		73.63
79	48	55.14	
82	35		70.80

Mixture $(a)^7$ is 0.13M in KCl.

Mixture $(c)^4$ is 0.0128M in $K_4Fe(CN)_6$.

Table 34.(2)

a = b = 0.0425M pH = 7.40 μ = 2.00 Temperature = 35.0°C

Time.		% $Na_2S_2O_3$ remaining.	
		Mixture (a)[8]	Mixture (c)[5]
Omins.	Osecs.	100.00	100.00
1	25	95.11	
3	51	91.78	
4	47		98.85
9	30		97.93
11	21	84.62	
13	48		95.88
15	57	81.57	
16	16		94.94
19	1		94.39
25	3		91.69
25	59	74.70	
32	15		88.15
35	59	69.64	
38	14		85.08
40	1		84.90
45	29		82.75
46	3	64.49	
49	40		80.98
56	19	61.15	
59	45		76.79
66	34	56.96	
79	15		71.40
79	55	52.85	

Mixture (a)[8] is 0.17M in KCl.

Mixture (c)[5] is 0.017M in $K_4Fe(CN)_6$.

Table 35.(2)

a = b = 0.0425M pH = 7.40 μ = 3.11 Temperature = 35.0°C

Time.		% $Na_2S_2O_3$ remaining.
		Mixture $(c)^6$
Omins.	Osecs.	100.00
4	56	99.51
6	53	98.57
10	27	97.09
13	44	94.83
14	55	93.25
22	52	86.89
30	6	82.49
45	49	72.67
60	2	67.16
82	33	60.13

Mixture $(c)^6$ is 0.128M in $K_4Fe(CN)_6$.

(4) The effect of ionic strength on the reaction.

The preliminary experiments described in Chapter 1. Section 2.11 have shown that the reaction is considerably accelerated by an increase in the ionic strength of the reaction medium. Use has been made of this knowledge in order to show more clearly the retarding and accelerating effects of the ferrocyanide and tetrathionate ions respectively. The results of that work are given in Chapter 2. Section 2.2 and 2.3.

Another series of experiments was performed in order to make certain that the accelerating effect observed when potassium chloride was added to the reaction mixture, was in fact due to a salt effect and not to a specific action of the potassium ion.

Mixtures of sodium thiosulphate and potassium ferricyanide were prepared and varying amounts of standard solutions of either potassium chloride or calcium chloride were added. The rates of the reactions were followed in the usual way.

Granular calcium chloride was used in this work, since the crystalline hydrated compound was too deliquescent to be dealt with conveniently. The pH of the borax-boric acid buffer solution used in these experiments, was shown to be unaffected by the calcium chloride solution.

The results of this work showed that the reaction

velocity depends upon the ionic strength; a large positive primary salt effect was observed, as would be expected from the Broensted intermediate complex theory.* (See Chapter 1. Section 2.11) Also, since the effect of adding calcium chloride was equal to that of adding an amount of potassium chloride such as to give the same ionic strength, the increase in velocity observed on the addition of potassium chloride cannot be due to some specific effect of the potassium ion.

Since the reaction proceeds at a readily measurable rate only in solutions of fairly high ionic strength no unambiguous conclusions can be drawn from the variation of the rate with ionic strength other than that the reaction occurs between species with similarly charged ions. An indication of the states of the ions which are concerned in the process may be obtained, however, by the following argument.

Suppose the ferricyanide and thiosulphate ions are in equilibrium with the ion pair or ion aggregate species which are actually concerned in the rate determining process according to the schemes

$$nX^{+} + Fe(CN)_6^{'''} \rightleftharpoons X_nFe(CN)_6^{-(3-n)} \qquad (A)$$

$$mX^{+} + S_2O_3^{''} \rightleftharpoons X_mS_2O_3^{-(2-m)} \qquad (B)$$

where X^{+} is any positive ion present, i.e. hydrogen, potassium or sodium ions.

* Some of these results are shown in Table 36.(2)

Then $a_A = k_1 a_{X^+}^{n} \cdot a_{Fe(CN)_6}^{'''}$ and $a_B = k_2 a_{X^+}^{m} a_{S_2O_3}^{''}$

where a_A etc. are the activities of the various ions.

Then the rate of the reaction will be proportional to the concentration of the transition state complex AB,

i.e. proportional to $a_A a_B / f_{AB}$

But this will be proportional to

$$a_X^{n} \cdot a_{Fe(CN)_6}^{'''} \cdot a_X^{m} \cdot a_{S_2O_3}^{''} / f_{AB} =$$

$$c_X^{m+n} \cdot c_{Fe(CN)_6}^{'''} \cdot c_{S_2O_3}^{''} \cdot f_X^{m+n} \cdot f_{Fe(CN)_6}^{'''} \cdot f_{S_2O_3} / f_{AB}$$

But the activity coefficient term F, is

$$f_X^{m+n} \cdot f_{Fe(CN)_6}^{'''} \cdot f_{S_2O_3}^{''} / f_{AB}$$

which is given by

$$\log F = (m+n)\log f_X + \log f_{Fe(CN)_6}^{'''} + \log f_{S2O_3}^{''} - \log f_{AB}$$

The charge on the complex AB will be 5-(n+m), so if the Debye Huckel limiting law held we would have

$$\log F = \sqrt{\mu}\left\{-(m+n)0.5 - 4.5 - 2 + (5-n-m)^2 0.5\right\}$$

If m and n are both zero this expression reduces to

$$\log F = 6\sqrt{\mu}$$

such as would be expected for a reaction between species carrying three and two like charges respectively. If, however, n+m=1 i.e. one is zero and the other is unity

$$\log F = \sqrt{\mu}$$

Higher values of n-m lead to large negative values of log F, indicating a negative solvent effect at low ionic strengths. As the positive salt effect is so great it seems improbable that there is a complete reversal at lower ionic strengths, so the evidence suggests that only one of the reacting species can be in an ion pair state. Further since the rates at equal ionic strength are the same when potassium chloride is replaced by calcium chloride, it seems improbable that an alkali metal ion is concerned in any ion pair. Hence it is more likely that the reactant species may involve the ion pairs formed with hydrogen ions; or only partially dissociated acids.

The salt effect suggests then that either the free ions $Fe(CN)_6^{'''}$ and $S_2O_3^{''}$ or one of these ions in the free state and the other in the form $HS_2O_3^{'}$ or $HFe(CN)_6^{''}$ are concerned. A rough indication of which of these alternatives is correct can be obtained by assuming ideality of behaviour in spite of the very high concentrations and ionic strengths involved. If we write the rate constant at ionic strength μ in the form $k_\mu = k_o F_\mu$

then $\log k_\mu = \log k_o + \log F_\mu = \log k_o + x\sqrt{\mu}$

Hence a plot of log k against $\sqrt{\mu}$ should be linear, the slope giving the value of x. The relative rates of reaction, as given by the reciprocals of the time required for the reaction to reach 70% completion, vary with ionic strength

as shown below.

μ	0.42	0.79	1.42	2.42
Relative rate.	1	2.1	4.6	12.2
$\log_{10}$(Rate)	0.00	0.322	0.663	1.086
$\sqrt{\mu}$	0.65	0.89	1.19	1.56

The slope of the $\sqrt{\mu}$ -$\log_{10}$(Rate) line is actually about 1.1, suggesting that x should have the value unity rather than 6.

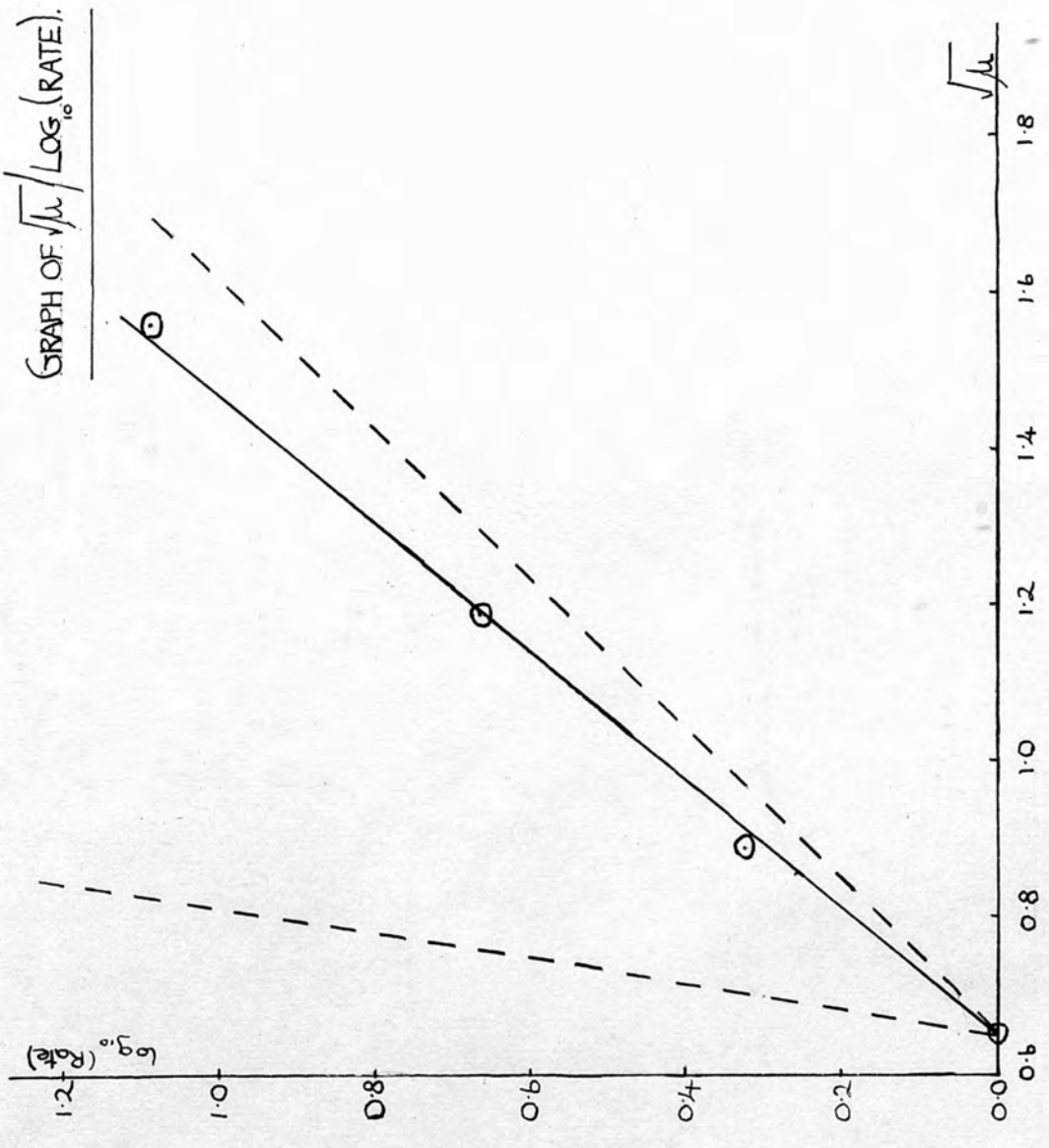

GRAPH OF $\sqrt{\mu}$ / LOG$_{10}$ (RATE).
log$_{10}$ (Rate)
1·2
1·0
0·8
0·6
0·4
0·2
0·0
0·6
0·8
1·0
1·2
1·4
1·6
1·8
$\sqrt{\mu}$

FIGURE 20

Table 36.(2)

a = 0.025M b = 0.05M pH = 7.40 Temperature = 35.0°C.

(a)

KCl = 0.0M μ = 0.42

Time.	% $Na_2S_2O_3$ remaining.
0 mins.	100.00
1 1/2	96.71
9	91.78
18	88.29
33	83.06
79	72.79
100	69.57
115	67.25

(b)

KCl = 0.366M μ = 0.79

Time.	% $Na_2S_2O_3$ remaining.
0mins.	100.00
2	93.41
9	85.74
17	81.40
28	77.33
44	70.66
65	61.82
83	54.65

(c)

KCl = 1.0M μ = 1.42

Time.	% $Na_2S_2O_3$ remaining.
0 mins.	100.00
1 1/2	89.92
8	78.68
18	71.71
28	65.43
39	57.36
54	46.90
105	22.09

(d)

KCl = 2.0M μ = 2.42

Time.	% $Na_2S_2O_3$ remaining.
0 mins.	100.00
1 1/2	81.01
6	74.69
12	68.22
19	61.24
26	53.49
31	47.67
37	39.15

(e)

$CaCl_2$ = 0.25M

μ = 1.17

Time.	% $Na_2S_2O_3$ remaining.
0 mins.	100.00
1 1/2	95.35
7	87.71
20	79.84
43	68.60
69	58.91
106	47.67

CHAPTER 3.

pH MEASUREMENTS.

Section 1.

Practical method used in pH measurement.

The majority of the measurements that have been made on the reaction between potassium ferricyanide and sodium thiosulphate have been carried out in buffer solutions. Various different mixtures were used for this purpose, according to the pH required:-

(a) Disodium hydrogen phosphate and potassium dihydrogen phosphate.

(b) Borax and boric acid.

(c) Boric acid with potassium chloride and sodium hydroxide.

The preparation of the mixtures is described in Chapter 3. Section 3.

Owing to secondary salt effects the pH of buffer solutions does depend upon the ionic strength of the reaction medium. Since the ionic strengths of the solutions used in the present work were always high, it was decided to measure the pH values of the buffered reaction mixtures.

The measurements were made with a Cambridge pH meter, in conjunction with a glass electrode and a calomel electrode. Where the pH of the mixture was likely to be greater than 9 units, a special 'Alki' glass electrode was used instead of the ordinary type employed in other measurements.

The calomel electrode was contained in a glass vessel as shown in Fig. 21. This type of container was used in

order to avoid the need for a salt bridge. The electrode was prepared by putting about 2mls. of purified mercury into tube A and then covering it with a paste of calomel.

This paste was made up from freshly precipitated mercurous chloride and mercury. The former was prepared by adding dilute hydrochloric acid to a dilute solution of mercurous nitrate in equilibrium with mercury. The precipitate was washed six times by decantation with a saturated solution of potassium chloride. The solid was then ground up in a mortar with a little mercury and a few drops of saturated potassium chloride solution. Finally this paste was washed three times with saturated potassium chloride solution, and a very thin layer was placed on the mercury in tube A. The remainder of the cell was then filled with saturated potassium chloride solution.(13)

A small piece of platinum wire sealed into a piece of glass tubing full of mercury was supported in tube A, so that the wire was submerged completely under the mercury and did not come into contact with the calomel paste.

The pH meter was connected up to the main voltage supply for at least half an hour before use to ensure that the valve system was heated adequately.

When the pH of a mixture was to be measured the meter was first set against a standard buffer solution. The electrode system was always immersed in each solution for

three minutes before a measurement was made. The standardising buffer, in the majority of cases, was the buffer solution that had been used for the kinetic experiment, diluted with an amount of distilled water equivalent to the volume of standard solutions used previously. This ensured that the glass electrode was immersed to the same depth in both the standardising buffer and the solution, the pH of which was to be measured. In a few cases where the 'Alki' electrode was being used, the meter was set against a solution of buffer tablets provided by the Cambridge Instrument Company for the purpose.

All these measurements were made in a thermostat where the conditions were identical with those under which the kinetic runs had been carried out. After the pH of the mixture had been read the glass and calomel electrodes were replaced in the standard buffer solutions and the setting of the meter was checked. When the pH of this standard appeared to have altered by amounts greater than 0.05 units, the reading was rejected.

The value of the pH of any mixture was found from an average of seven or eight readings taken over a period of about seven hours.

Table 1.[3]

No. of reaction mixture.	pH value of standard buffer solution.	Type of electrode.	Measured pH value of reaction mixture.
1	5.91	A	5.53
2	6.64	A	6.25
3	7.38	A	6.97
4	7.73	A	7.21
5	7.78	A	7.40
6	8.34	A	8.21
7	8.48	A	8.31
8	8.77	A	8.62
9	9.11	B	8.97
10	9.11	B	8.98
11	9.11	B	9.00

A is the normal glass electrode.

B is the 'Alki' glass electrode.

(Details of the standard buffer solutions are given in section 3 of this chapter.)

Section 2.

pH measurements on an unbuffered reacting mixture.

It had been noticed that when the reaction mixture was buffered, the abnormalities apparent in the unbuffered mixture were very much less pronounced. (See Chapter 1.Section2.6) It therefore seemed possible that these unusual features were caused by a change in the pH of the mixture during the reaction. It was decided, in view of this, to measure the pH of the unbuffered reacting mixture during a kinetic run.

A graph of the change of pH with time, under these conditions and at 30°C, shows that in the first one and three quarter hours the pH value of the mixture drops by rather more than 0.3units, after which it rises by 0.7units in the next five hours, to reach a maximum. These results are shown in Table 2.(3)

The pH meter was set against a standard buffer mixture of pH 5.59. This is described in Chapter 3. Section 3. Measurements were made as described in the previous section. A normal glass electrode was used.

If these pH values are compared with the rate of the reaction in the same conditions, it can be seen that the initial period of rapid reaction followed by the longer period of retardation, occurs while the pH of the mixture is falling. As the pH of the mixture begins to rise once more, the final period of acceleration is occurring. A graph showing the

variation of pH with the percentage reaction is given in Fig. 22.

It was impossible to obtain steady readings from the pH meter during the first half hour of the reaction. It is during this time that the initial rapid reaction is taking place.

Table 2.[3]

a = b = 0.0425M Unbuffered solution. Temperature = 30.0°C

Time.	% reaction.	Measured pH value of the mixture.
0hrs. 0mins.	0.00	
0 4	2.17	
0 9	4.35	
0 15	4.71	
0 19		5.71
0 28	7.07	
0 40		5.58
0 43	8.34	
1 3	10.07	
1 11		5.49
1 28		5.44
1 42		5.40
1 43	14.52	
1 56		5.42
2 13	17.24	
2 52		5.65
2 58	23.60	
3 56	30.23	
4 9		5.97
4 55	38.23	6.03
5 58	47.04	
6 16		6.08
6 58	53.13	
7 27		6.10
7 31	55.76	

THE CALOMEL ELECTRODE CONTAINER.

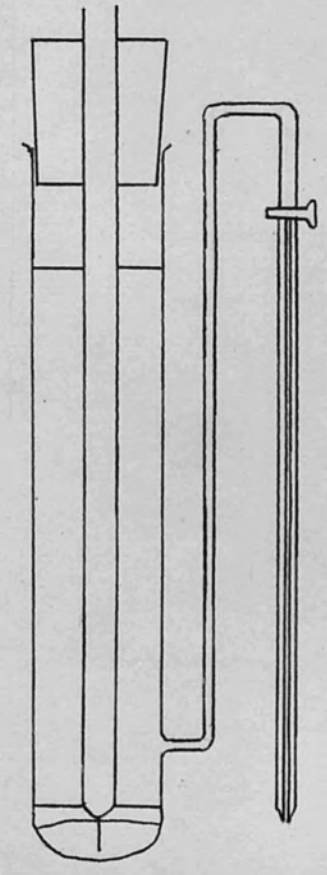


FIGURE 21.

GRAPH TO SHOW THE VARIATION OF pH WITH % REACTION.

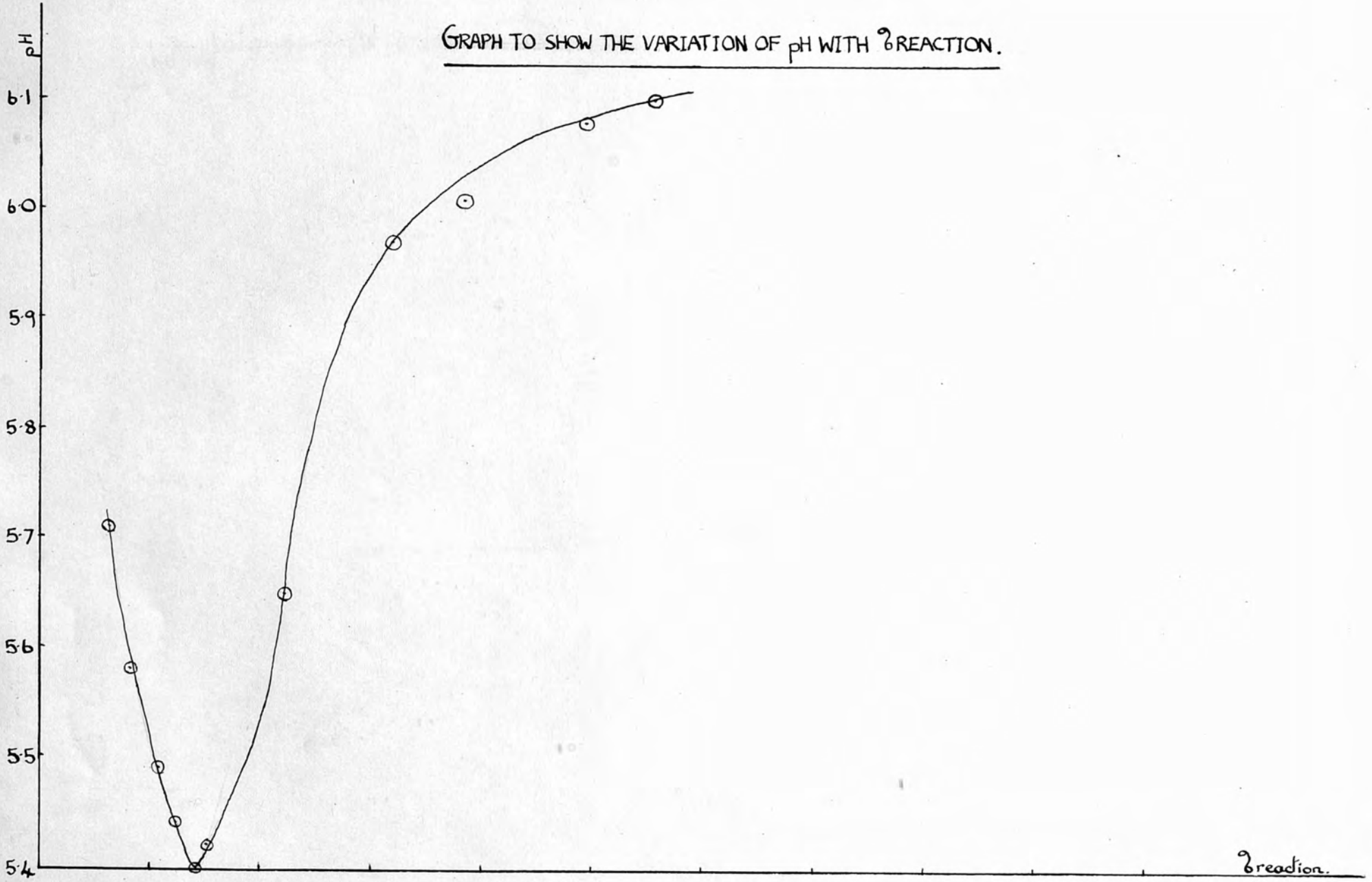


FIGURE 22.

Section 3.

Buffer solutions.

A series of different buffer solutions were used in this work, so that the characteristics of the reaction between potassium ferricyanide and sodium thiosulphate could be studied over a range of pH values.

The buffer solutions used for the preliminary experiments described in Chapter 1. Section 6. were prepared from 0.1N solutions of sodium dihydrogen phosphate and disodium hydrogen phosphate. The composition of these mixtures is given in Table 3.(3)

The accurate experiments carried out at pH values below 7.2, were again buffered with phosphate solutions. However, in this part of the work, mixtures of M/15 solutions of disodium hydrogen phosphate ($Na_2HPO_4.\ 12H_2O$) and potassium dihydrogen phosphate (KH_2PO_4) were used.(14,15) The reagents were both of 'Analar' grade. Details of these mixtures are given in Table 4.(3)

Some measurements were made in solutions buffered with a mixture of borax, boric acid and sodium chloride.(16)

The borax used for this work was recrystallised from A.R. grade borax by dissolving it in distilled water, using 50mls. of water for every 15g. of borax; the solution was then filtered and left to cool. Care was taken to see that crystallisation occurred at a temperature below 55°C. The

crystals were filtered off and washed twice with water and twice with ether, using approximately 5mls. of wash liquid for every 10g. of borax crystals. Finally the borax was spread thinly on filter papers and left to dry at room temperature for eighteen hours.

The boric acid used in this and other buffer mixtures was also recrystallised. Powdered boric acid was dissolved in boiling water, using 100mls. of water for each 20g. of boric acid. After filtration the boric acid was allowed to crystallise out. It was then filtered off and dried in air.

Details of the solutions used in this buffer mixture are given in Table 5.[3]

When a more alkaline buffer solution was required it was prepared from an approximately 0.2N sodium hydroxide solution and a solution containing boric acid and potassium chloride.(See Table 6)[3][17] The potassium chloride used was 'Analar' grade. The sodium hydroxide solution was prepared from pellets of this compound, rinsed and dissolved in distilled water. This solution was then standardised using 'Analar' grade potassium hydrogen phthalate, which was oven dried and cooled before use. About 0.7g. of this compound was weighed out accurately into a conical flask immediately before use. Then about 75mls. of distilled water were added and when the solid had dissolved the solution was titrated against the sodium hydroxide solution, using phenol phthalein

as an indicator.

For the kinetic runs carried out at a pH of approximately 11.24, a mixture of disodium hydrogen phosphate solution and sodium hydroxide solution was used.[21] Details of this mixture are given in Table 7.[3]

Table 3.[3]

Vol. of Na_2HPO_4 soln.	Vol. of NaH_2PO_4 soln.	pH
1ml.	50mls.	5.5
2	20	6.2
20	10	7.5

Table 4.[3]

M/15 $Na_2HPO_4.12H_2O$.	M/15 KH_2PO_4.	Theoretical pH value.[14]	Measured pH of buffered mixture.
8mls.	2mls.	7.38	7.21
9	1	7.73	6.97
4	6	6.64	6.25
1	9	5.91	5.53

Table 5.[3]

M/20 borax.	M/5 boric acid, sodium chloride.	Theoretical pH value(16)	Measured pH of buffered mixture.
2mls.	8mls.	7.78	7.40

Table 6.[3]

50mls. of a solution containing 12.3688g. H_3BO_3 and 14.9110g. KCl per litre, were used in each mixture.

Vol. NaOH soln.	Normality of NaOH soln.	Theoretical pH value(17)	Measured pH of buffered mixture.
7mls.	0.224M	8.34	8.21
10	0.197	8.48	8.31
14	0.224	8.77	8.62
30	0.187	9.25	8.97
25	0.243	9.33	8.98
40	0.197	9.73	9.00

Table 7.[3]

0.15M Na_2HPO_4	0.092M NaOH.	Theoretical pH value(21)	Measured pH of buffered mixture.
50mls.	25mls.	11.24	

CHAPTER 4.

DISCUSSION OF THE RESULTS OBTAINED.

Section 1.

Summary of general conclusions.

The major results may be summarised as follows.

A. Unbuffered solutions.

In solutions containing equimolecular concentrations of potassium ferricyanide and sodium thiosulphate, the concentration of thiosulphate falls rapidly during the first few minutes after mixing. This is followed by a considerably longer period of appreciably slower reaction, and this in turn is succeeded by a slight acceleration and a more normal type of reaction curve. The reaction tends to become slower than expected however, in the final stages, probably owing to the fact that the reaction does not go quite to completion.

This general form of reaction curve is reproducible and seems to be independent of the initial concentrations of both potassium ferricyanide and sodium thiosulphate. Further, it is unaltered by further purification of the potassium ferricyanide, by the exclusion of oxygen or by the additions of small concentrations of cyanide. It seems improbable, therefore, that the curious form of the reaction curve is associated with the intervention of oxygen or with the products of hydrolysis of the ferricyanide or ferrocyanide ions. Small amounts of added ferric ion modify the rate of the initial reaction but this seems more likely to be produced through the consequent change in the pH of the solution through hydrolysis of the

ferric ion than through any specific effect of that ion.

Small amounts of potassium ferrocyanide added to the initial reaction mixture produce a marked retardation in the early stages of the reaction, giving the effect of an induction period.

The initial period of rapid reaction followed by the longer period of retardation is accompanied by a decrease in the pH of the solution, whilst the subsequent period of acceleration is accompanied by an increase in the pH.

B. Buffered solutions.

When the reacting mixture is buffered the reaction curve is partially smoothed, but a slight initial period of more rapid reaction still persists. The reaction shows a strong positive salt effect, the acceleration produced by potassium chloride addition being equal to that produced by the presence of sufficient calcium chloride to give the same ionic strength. This suggests that if ion pairs are concerned in the reaction only one of the reactants can be in such a state and that the one concerned must be either of the form $XFe(CN)_6''$ or XS_2O_3', where X is not potassium.

Potassium ferrocyanide additions to the reaction mixture produce the same retarding effect as in the unbuffered solutions. This is masked to some extent by the salt effect but, at constant ionic strength, the retardation produced by a small initial concentration of ferrocyanide ion is

proportional to that concentration. This finding is in conflict with the observations by Sandved and Holte[5] who inferred that ferrocyanide merely removes some of the initial complications. Actually its effect is greatest in the initial stages of the reaction and it can cause very considerable retardation.

Sodium tetrathionate causes a marked acceleration of the early stages of the reaction but the effects of the initial additions become less marked as the reaction proceeds. In accordance with this observation the accelerating effect of the tetrathionate ion seems to tend to a limiting value as its initial concentration is increased.

Section 2.

Discussion of the results.

(1) Introduction.

Any mechanism proposed for the reaction between sodium thiosulphate and potassium ferricyanide should explain the following features of its kinetics.

(a) The large accelerating effect of sodium tetrathionate at the beginning of the reaction and its lack of strong effect towards the end of the reaction.

(b) The retarding effect of potassium ferrocyanide, most pronounced in the initial stages of the reaction but persisting to a lesser extent throughout the reaction.

(c) The large primary salt effect observed.

(d) The fact that after certain initial irregularities the reaction follows a second order law in neutral or slightly alkaline solution, but shows an increasing tendency towards first order kinetics in acid solution.

(e) The observation that in unbuffered solutions an initial rapid reaction is followed by a period of retardation and then a period of further acceleration, features which become less marked when the reaction occurs in a buffered solution.

(f) The changes which occur in the pH value when the reaction takes place in unbuffered solution, and their relationships to the anomalous course of the early stages of the reaction

in unbuffered solutions.

(2) The nature of the reacting species.

Since the additions of either ferric ions or cyanide ions produce no appreciable change in the reaction velocity it is unlikely that any major part in the reaction is taken by ferricyanide ions that have dissociated according to the equation

$$Fe(CN)_6^{'''} \rightleftharpoons Fe^{+++} + 6(CN)^{'}$$

or which have undergone hydrolysis to give any one of the series of complex ions of the type $Fe(CN)_5(OH)^{'''}$. Hence one of the species involved in the primary reaction is almost certainly $Fe(CN)_6^{'''}$ or an ion of the type $HFe(CN)_6^{''}$. Ion pairs involving alkali metal ions seem improbable, since the relative effects of additions of potassium and calcium ions would not in that case follow exactly the changes in ionic strength which they produce.

No formation of sulphur is apparent during the reaction at pH values of 6 and above, excepting for a negligable amount which appears after the reaction products have been kept for a prolonged time. Hence the thiosulphate ion is probably not dissociated in any way into sulphite or similar ions through reactions of the type

$$S_2O_3^{''} \rightleftharpoons S + SO_3^{''}$$

It must be inferred therefore, that the second reacting

species is the $S_2O_3^{''}$ ion or the $HS_2O_3^{'}$ ion.

When discussing the effect of ionic strength on the system it was pointed out that the existence of a strong positive primary salt effect indicates that both the reacting species cannot be in the ion pair (or incompletely dissociated) state, but that the magnitude of the salt effect favours the view that one of the reactants is in such a state. For reasons which will be discussed later the view favoured is that $Fe(CN)_6^{'''}$ and $HS_2O_3^{'}$ are the species concerned.

The obvious complexity of the reaction has rendered the determination of an activation energy rather meaningless, but roughly speaking it has been found that the rate is doubled on raising the temperature from 25°C to 35°C, suggesting a relatively low activation energy of the order of 13kcals.

A very slow reaction generally arises because either (a) the activation energy is high or (b) one of the reacting species is present at low concentration. It seems likely therefore, that in the present instance the latter is the case, giving still further evidence that one of the reactants is a species of the type $HS_2O_3^{'}$.

(3) A general discussion of the mechanism of the reaction.

Following the usual conception of the mechanism of reductions by thiosulphate ions, Sandved and Holte formulated the reaction as

$$Fe(CN)_6^{'''} + S_2O_3^{''} \longrightarrow Fe(CN)_6^{''''} + S_2O_3^{'}$$

$$2S_2O_3^{'} \longrightarrow S_4O_6^{''}$$

In view of the retarding effect of potassium ferrocyanide on the reaction, it seems most probable that the first stage of the process is reversible, the back reaction proceeding at an appreciable rate in the presence of high concentrations of ferrocyanide ion.

Again the considerable increase in reaction velocity occurring when sodium tetrathionate is added to the inital mixture of sodium thiosulphate and potassium ferricyanide suggests that a second primary step, involving the participation of tetrathionate ions, may provide an alternative and more rapid path for the reaction. As this accelerating effect is suppressed by the simultaneous addition of potassium ferrocyanide, the process involved must also be reversible. A possible step would therefore be

$$Fe(CN)_6^{'''} + S_4O_6^{''} \rightleftharpoons Fe(CN)_6^{''''} + S_4O_6^{'}$$

Removal of the $S_2O_3^{'}$ and $S_4O_6^{'}$ radicals must be accomplished in later steps of the reaction. In the case of

the S_4O_6' radical it seems probable that the reaction occurs with a thiosulphate ion, giving tetrathionate ions and S_2O_3' radicals. There seems no alternative to the usually accepted dimerization process to account for the disappearance of S_2O_3' radicals. Further it seems most probable that the two last reactions can be regarded as effectively irreversible.

Without reference, at the moment, to the precise form of the ions involved, i.e. whether they are $Fe(CN)_6'''$ or $HFe(CN)_6''$, S_2O_3'' or HS_2O_3', $Fe(CN)_6''''$ or $HFe(CN)_6'''$ etc., but concentrating rather upon the oxidation states involved, a possible mechanism for the reaction between ferricyanide and thiosulphate ions assumes the form

$$Fe(CN)_6''' + S_2O_3'' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(CN)_6'''' + S_2O_3' \qquad (1)$$

$$Fe(CN)_6''' + S_4O_6'' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe(CN)_6'''' + S_4O_6' \qquad (2)$$

$$S_4O_6' + S_2O_3'' \xrightarrow{k_3} S_2O_3' + S_4O_6'' \qquad (3)$$

$$2\,S_2O_3' \xrightarrow{k_4} S_4O_6'' \qquad (4)$$

For brevity the concentrations of the various species present at any instant will be denoted as follows:-

$$\left[Fe(CN)_6'''\right] = A \qquad \left[S_2O_3''\right] = B \qquad \left[Fe(CN)_6''''\right] = C$$

$$\left[S_2O_3'\right] = D \qquad \left[S_4O_6''\right] = E \qquad \left[S_4O_6'\right] = F$$

The rate constants of the forward reactions will be indicated

by k_1, k_2, k_3 and k_4 and those of the two back reactions by k_{-1} and k_{-2}.

Application of the steady state condition gives

$$\frac{dF}{dt} = AEk_2 - CFk_{-2} - BFk_3 = 0$$

$$\text{Hence } F = \frac{AEk_2}{Ck_{-2} + Bk_3} \tag{5}$$

$$\text{Similarly } \frac{dD}{dt} = ABk_1 - CDk_{-1} + BFk_3 - D^2k_4 = 0$$

$$\text{Whence } D = \frac{-Ck_{-1} + \sqrt{C^2k_{-1}^2 + 4ABk_1k_4 + 4BFk_3k_4}}{2k_4}$$

$$= \frac{-Ck_{-1} + \sqrt{C^2k_{-1}^2 + 4ABk_1k_4 + 4Bk_3k_4\left(\frac{AEk_2}{Ck_{-2} + Bk_3}\right)}}{2k_4} \tag{6}$$

The rate of the reaction as measured is given by

$$-\frac{dB}{dt} = ABk_1 - CDk_{-1} + BFk_3 \tag{7}$$

Substitution of the values of D and F from equations (6) and (5) into this rate equation (7) gives

$$-dB/dt =$$

$$ABk_1 + AEk_2\frac{Bk_3}{Ck_{-2} + Bk_3} + \frac{Ck_{-1}}{2k_4}\left[Ck_{-1} - \sqrt{C^2k_{-1}^2 + 4ABk_1k_4 + 4Bk_3k_4\frac{AEk_2}{Ck_{-2} + Bk_3}}\right] \tag{8}$$

It has already been mentioned that it seems likely that the ion actually involved in the first step of the

reaction is $HS_2O_3^{'}$. The second dissociation constant of thiosulphuric acid is about $1x10^{-2}$ at 25°(Landholt-Bornstein Tabellen)[23] and hence at pH values of the order of 8 the concentration of these ions is small, but finite, and is given by

$$\left[S_2O_3^{''}\right]\left[H_3O^{+}\right] / \left[HSO_3^{'}\right] = 10^{-2}$$

$$\text{or } \left[H_2SO_3^{'}\right] = \left[S_2O_3^{''}\right]\left[H_3O^{+}\right] x10^{2}$$

Under all conditions encountered in this work the concentration of $S_2O_3^{''}$ ions can be taken as sensibly equal to the total thiosulphate concentration, and hence the $HS_2O_3^{'}$ concentration at any particular pH value is directly proportional to the thiosulphate concentration.

The fate of the proton in this primary step is a matter for conjecture, but rather more important is the question of whether a proton containing ion is involved in the reverse step of either reaction (1) or reaction (2). The fourth dissociation constant of ferrocyanic acid is $5x10^{-5}$, whilst its third dissociation constant is about 10^{-3}. [25,24] Hence the concentration of $HFe(CN)_6^{'''}$ ions will be quite significant at most pH values at which the reaction was investigated. It is not improbable, therefore, that both the reverse reactions may involve this ion, the concentration of which will be given by

$$\left[HFe(CN)_6^{'''}\right] = \left[Fe(CN)_6^{''''}\right]\left[H_3O^{+}\right] x2x10^{4}$$

Excepting at the very lowest pH values this can be taken as proportional to the total ferrocyanide concentration.

Since the indirect reaction involving the tetrathionate ion appears to occur more readily than the direct reaction, and to persist at high pH values where the direct reaction becomes very slow, it seems probable at first sight that the forward reaction (2) involves the S_4O_6'' ion and not the HS_4O_6' ion. There appear to be no recorded values of the dissociation constants of tetrathionic acid and owing to the instability of the free acid it would be difficult to determine, but it will be shown that the variation of the rate of the reaction with pH is most easily explained by assuming that the reaction (2) also takes place through HS_4O_6' ions.

Assuming that the reactions (1) and (2) should be replaced by

$$Fe(CN)_6''' + HS_2O_3' \rightleftharpoons HFe(CN)_6''' + S_2O_3' \qquad (9)$$

$$Fe(CN)_6''' + HS_4O_6' \rightleftharpoons HFe(CN)_6''' + S_4O_6' \qquad (10)$$

the general rate equation assumes exactly the same form as equation (8) but with

k_1 replaced by $k_9 \times [H_3O^+] \times 10^2$

k_{-1} replaced by $k_{-9} \times [H_3O^+] \times 2 \times 10^4$

k_2 replaced by $k_{10} \times [H_3O^+] \times K$

and k_{-2} replaced by $k_{10} \times \left[H_3O^+\right] \times 2 \times 10^4$

where K is the association constant for the formation of HS_4O_6' ions, assumed to be relatively small.

If these assumptions are correct, it is permissible, in discussing the reaction at any particular pH value, to retain the general form of equation (8), whilst bearing in mind the possible dependence of k_1, k_{-1} and k_2 and k_{-2} upon the pH value.

As it stands this equation is still too cumbersome for convenient analysis. Some simplification can be effected, however, by writing

$$X = ABk_1 + AEk_2 \frac{Bk_3}{Ck_{-2} + Bk_3}$$

If there were no 'indirect' reaction through the intervention of tetrathionate ions this function X would be replaced by ABk_1. Its divergence from this value can be expressed simply by writing

$$X = ABk_1\left(1 + \frac{k_2}{k_1} \frac{E}{Ck_{-2}/k_3 + B}\right)$$

The relative importance of the two reactions evidently depends on the ratios $k_2:k_1$ and $k_{-2}:k_3$. Let these be r_1 and r_2 respectively, so that

$$X = ABk_1\left(1 + \frac{r_1E}{r_2C + B}\right) = ABk_1Y \qquad (11)$$

where $Y = 1 + \frac{r_1 E}{r_2 C + B}$ (12)

Introducing this notation into the general rate expression (8) and rearranging to emphasise the retarding significance of the last term we obtain

$$-\frac{dB}{dt} = ABk_1Y - \frac{Ck_{-1}}{2k_4}\left(\sqrt{C^2k_{-1}^2 + 4ABk_1k_4Y} - Ck_{-1}\right)$$

$$= ABk_1Y - \frac{Ck_{-1}}{\sqrt{k_4}}\left[\sqrt{\frac{(Ck_{-1})^2}{4k_4} + ABk_1Y} - \frac{Ck_{-1}}{2\sqrt{k_4}}\right]$$

$$= ABk_1\left[Y - \frac{Ck_{-1}}{(ABk_1k_4)^{1/2}}\left\{\sqrt{\frac{C^2k_{-1}^2}{4ABk_1k_4} + Y} - \frac{Ck_{-1}}{2(ABk_1k_4)^{1/2}}\right\}\right]$$

If the ratio $k_{-1} / 2k_1k_4$ is now written r_3 the equation reduces to

$$-\frac{dB}{dt} = ABk_1\left[Y - \frac{2Cr_3}{\sqrt{AB}}\left(\sqrt{\frac{C^2r_3^2}{AB} + Y} - \frac{Cr_3}{\sqrt{AB}}\right)\right] \quad (13)$$

Thus the reaction is to be expected to have essentially second order kinetics but with certain complications, the magnitudes of which will depend upon the extent to which Y departs from unity, and, especially in the later stages of the process, or in the presence of added ferrocyanide, upon the value of r_3.

It is interesting to note at this stage that replacing k_1 and k_{-1} by k_9 and k_{-9}

$$r_3 = \frac{k_{-9}}{2\sqrt{k_9 k_4}} \cdot \frac{\left[H_3O^+\right] \cdot 2\times10^4}{\left[H_3O^+\right]^{1/2} \cdot 10}$$

Hence r_3 would be expected to be proportional to the square root of the hydrogen ion concentration. Its actual magnitude is difficult to predict from first principles. The rate constant k_4 must be large because a dimerization of S_2O_3' radicals probably occurs also during the reduction of iodine by thiosulphate, which is known to be a fast reaction. At the same time the reverse reaction of process (1) must have a high rate constant, as otherwise no retardation would be produced by the back reaction.

Little can be said at the moment, therefore, other than that the last (retardation) term becomes increasingly important as the ratio $C / \sqrt{AB}$ increases and hence is particularly important towards the end of the reaction. This gives a general explanation of the observation that the second order plots depart from linearity towards the end of the reaction when the values of $1 / (p-x)$ tend to become anomalously low — the sense in which deviations are to be expected if there is a retardation term in the rate equation. Limits which must be imposed upon the value of the velocity constant ratio r_3 in certain specified conditions are dicussed later.

Before any further conclusions can be drawn about this

and other more detailed features of the kinetics, it is necessary to consider the parts played by the tetrathionate and ferrocyanide ions, which have been shown to accelerate and retard the reaction, respectively. It is also necessary to examine the implications of the observed variation of the kinetics of the reaction with the pH of the solution.

(4) The accelerating effect of tetrathionate ions.

It follows from equation (8) that in the initial stages of the reaction, when the concentration of the ferrocyanide ions is small, the reaction rate in the presence of added sodium tetrathionate should be given by

$$-\frac{dB}{dt} = ABk_1 + AEk_2$$

The reaction should therefore be more rapid than without the addition of tetrathionate, as is observed. It is very difficult to obtain the tangent to the curve of (p-x) against t at zero time, however, as at the pH value at which the effects of added tetrathionate were studied (7,40) the reaction seems to be very rapid in the initial stages, even at the lowest tetrathionate concentration used. Further the plot of 1 / (p-x) against t is curved from the start and hence the value of its slope at zero time is again impossible to obtain, particularly as there is an uncertainty as to the exact time at which the reaction should be regarded as beginning. The sense of the curvature of the 1 / (p-x) against t plot, however, is such as to suggest that the function Y in equation (13) diminishes fairly rapidly with time during the course of the reaction. If the initial concentrations of ferricyanide and thiosulphate are a, and the initial concentration of tetrathionate is ae, then when a fraction x of the reactants has disappeared the function Y is given by

$$Y = \frac{r_1 \left(e + \frac{x}{2}\right)}{r_2 x + 1 - x} \qquad (14)$$

It follows, therefore, that if Y is to decrease with time, i.e. with increasing extent to which the reaction has progressed, r_2 must be appreciably greater than unity. A value of unity or less would cause Y to increase progressively with time. It follows therefore, that at pH 7.40, k_{-2} must be appreciably greater than k_3, that is the S_4O_6' radicals react more readily with ferrocyanide ions (or $HFe(CN)_6'''$ ions) than they do with thiosulphate ions. This state of affairs is also borne out by the fact that, except during the very early stages of the reaction, the process in the absence of added tetrathionate ions shows very little departure from second order kinetics until the reaction is about 70% complete. The slope of the $1 / a(1-x)$ ~~$-t$~~ against t plot will then give the value of k_1Y, i.e. $k_1\left(1 + \frac{r_1}{2r_2}\right)$

The actual assignment of values to r_1 and r_2 is attended by considerable possible experimental error but some estimate of their relative values can be made. The slopes of the tangents to the $1 / (a-x)$ against t plots for the tetrathionate catalysed reaction are determined at times corresponding to various values of x, and are compared with the slopes of the corresponding plots for the reaction

mixture with the same pH, ionic strength and initial ferricyanide and thiosulphate concentrations as the mixture concerned, but without added tetrathionate ions. The results recorded in Table 27[2] and the corresponding 1 / (1-x) against t plots shown in Fig. 23 indicate that for a mixture 0.0425M both in sodium thiosulphate and in potassium ferricyanide, buffered to pH 7.40 and initially 0.0043M in sodium tetrathionate, the values of Y after the reaction is 6%, 10% and 16% complete are 1.56, 1.34 and 1.21 times the value for the reaction mixture to which no tetrathionate has been added. We can then write

$$1 + \frac{0.13r_1}{0.06r_2 + 0.94} = 1.56\left(1 + \frac{r_1}{2r_2}\right)$$

$$1 + \frac{0.15r_1}{0.10r_2 + 0.90} = 1.34\left(1 + \frac{r_1}{2r_2}\right)$$

$$1 + \frac{0.18r_1}{0.16r_2 + 0.90} = 1.21\left(1 + \frac{r_1}{2r_2}\right)$$

These equations, however, do not permit an unambiguous determination of r_1 and r_2, as the relative values of Y for the three values of x are almost exactly those which would be expected if r_2 were infinite. This can be illustrated by assuming various values for r_2, calculating the value of r_1 from the relative value of Y when $x = 0.06$, and thence

calculating the relative values of Y when x = 0.10 and 0.16. This leads to the following results:-

r_2	r_1	Relative value of Y.		
		x = 0.06	x = 0.10	x = 0.16
Very large.	$0.403r_2$	1.56	1.335	1.209
4000	$1628r_2$	1.56	1.337	1.212
1000	418.4^2r_2	1.56	1.340	1.214
100	$51.2r_2$	1.56	1.357	1.230
10	$8.73r_2$	1.56	1.471	1.358

Table 1.(4)

The ratios observed correspond most nearly to a value of at least 1000 for r_2 and 418.4 for r_1, but owing to the high experimental error r_2 may have any value above about 100. Analagous examination of the experimental results relating to larger initial additions of sodium tetrathionate lead to similar conclusions. It is evident, however, that the value of r_1 must lie between $0.4r_2$ and $0.5r_2$ indicating that over most of the course of the reaction Y is 1.2 to 1.25, i.e.between one fifth and a quarter of the reaction takes place through the indirect mechanism. When discussing the effect of pH value on the reaction rate it will be pointed out that the course of the reaction at pH 11 can be most easily reconciled with a value of r_2 of about 4000 at pH 7.40.

Assuming suitable values of r_1 and r_2 it is of some interest to note the way in which the function Y will vary with x in the absence of added tetrathionate as well as in its presence. The values to be expected if r_2 is 4000, 1000

or 100 are shown in Table 2 in this chapter. These indicate that, in accordance with the qualitative arguments already given, in the presence of added tetrathionate the value of Y decreases rapidly in the initial stages of the reaction and more gradually in the later stages, the rate of reaction towards the end of the process being almost of the form expected for a second order reaction. Similarly, when no tetrathionate is present initially the value of Y increases rapidly in the early stages of the reaction, but later becomes almost constant, so that the reaction will follow almost exactly a second order law until it is approaching completion when the retardation arising from the term $\frac{C}{\sqrt{AB}} r_3 \sqrt{Y}$ becomes significant. The steady condition of second order kinetics is attained at an earlier stage of the reaction the higher the value of r_2, and the fact that from about $x = 0.05$ onwards deviations from linearity in the $1 / (1-x)$ against t plot are not detectable is evidence that r_2 probably has a high value of the order of 1000 or greater.

The general rate equation, excluding the last (retardation) term actually predicts that there should be a maximum rate of reaction attained when

$$\frac{d}{dx}(1-x)^2\left\{1-\frac{r_1 x/2}{r_2 x + 1 - x}\right\} = 0$$

This can be written in the form

$$\frac{d}{dx}(1-x)^2\frac{(nx+1)}{mx+1} = 0$$

where $n = r_2 + 0.5r_1 - 1$ and $m = r_2 - 1$

which leads to the condition

$$x^2 + \left(\frac{3}{2m} + \frac{1}{2n}\right)x + \left(\frac{1}{2n} + \frac{1}{nm} - \frac{1}{2m}\right) = 0$$

For r_2 = 4000, 1000 and 100 this predicts maximum rates after about 0.6%, 1.7% and 3.5% completion, respectively. Although definite indication of a maximum rate was not detected at this pH value, evidence for such a maximum is given by the reaction-time curves for certain other conditions.

The relationship leads to the prediction that the acceleration produced by the addition of tetrathionate should be proportional to the amount added. The results seem to indicate that this is the case for small additions but that the rule tends to break down at higher concentrations. Under such conditions, however, the reaction becomes extremely rapid and hence the results, especially those relating to the early stages of the reaction, become less accurate, so no very definite conclusions can be reached on this point.

A result which remains to be accounted for is that relating to the experiment in which mixtures were made corresponding to the materials present when the reaction is two-thirds complete. Careful examination of the results shows that, excepting for the last measurements, which were at such an advanced stage of the reaction that the retardation term was significant, the 1 / 1-x against t plots would suggest

that the rate of reaction in these mixtures was only slightly greater when the sodium tetrathionate was added than when it was omitted. The figures given in Table 2[4] of this chapter suggest that if r_2 is 4000 or 1000 it should be 20% greater, whilst if r_2 is 100 it should be 25% greater with the tetrathionate than without it. It may be important to note, however, that the retardation term may be becoming fairly large when x = 0.7 or over and that this term increases with increasing value of Y. Hence the retardation term will be greater when the tetrathionate is added than when it is not, and this factor may account in part for the apparent discrepancy of the observation. It is rather significant to note in this connection that working at a lower pH value of 6.1, where the indirect mechanism seems to be still less important than at pH 7.40, and making mixtures corresponding to the half complete reaction-- conditions such that the retardation term would be less important--Sandved and Holte found that omission of the tetrathionate led to an apprecibly lower reaction rate than when it is present.

Table 2(4)

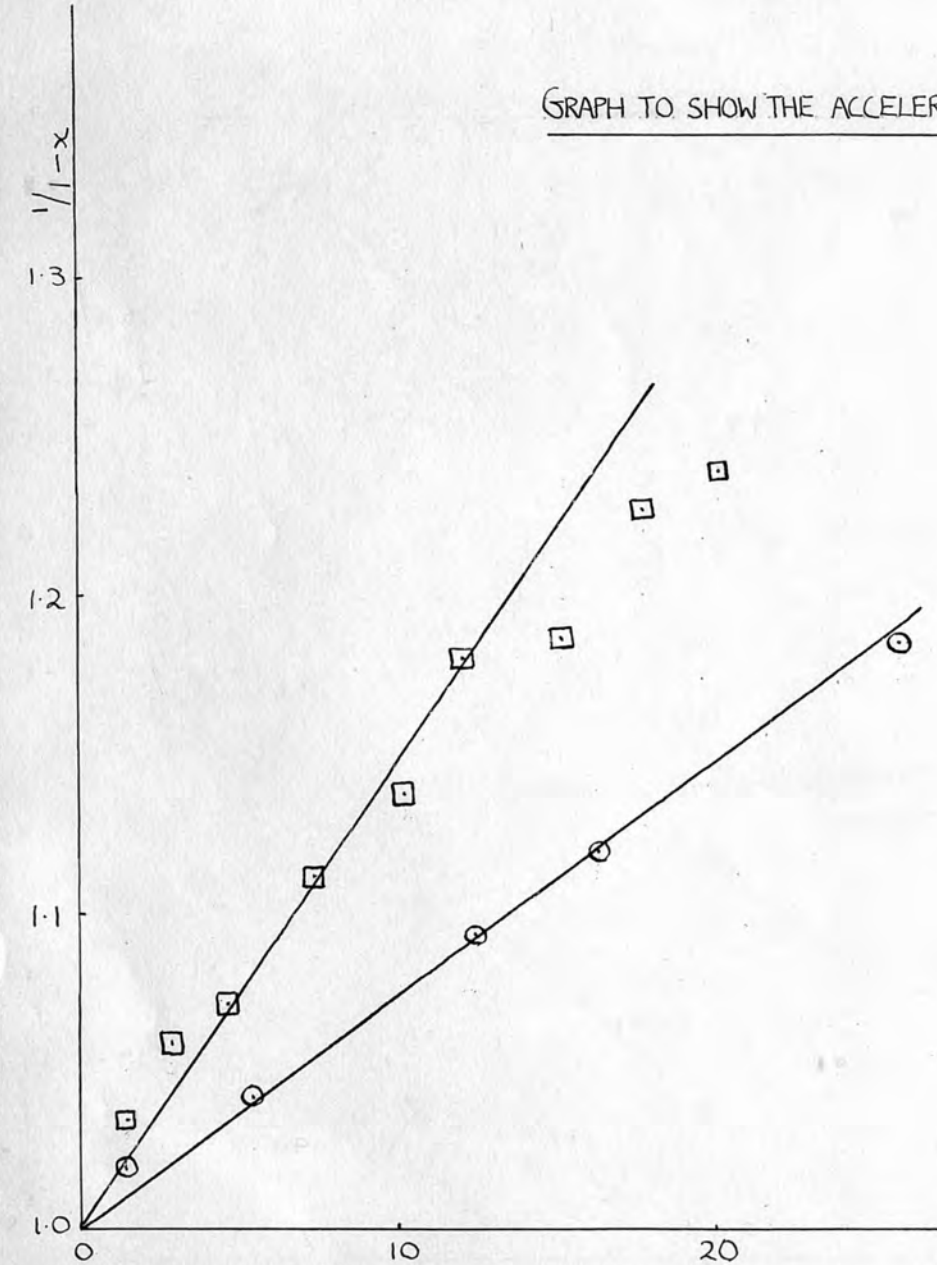
Values of Y for different values of x and r_2.

x	0.00	0.01	0.02	0.05	0.10	0.20	0.50	1.00
$r_2 = 4000$								
m_1	1.0	1.198	1.200	1.202	1.203	1.2032	1.2034	1.2035
n_1	162.8	5.41	3.21	2.12	1.609	1.406	1.285	1.244
m_1/n_1	162.8	4.51	2.67	1.76	1.34	1.168	1.068	1.034
$r_2 = 1000$								
m_2	1.0	1.192	1.199	1.205	1.207	1.208	1.2085	1.2092
n_2	42.84	4.99	3.19	2.02	1.621	1.417	1.292	1.251
m_2/n_2	42.84	4.19	2.66	1.67	1.34	1.17	1.07	1.03
$r_2 = 100$								
m_3	1.0	1.128	1.171	1.213	1.233	1.246	1.253	1.256
n_3	6.12	3.688	2.877	2.060	1.705	1.492	1.353	1.307
m_3/n_3	6.12	3.27	2.46	1.70	1.38	1.20	1.08	1.04

m = Y in absence of added S_4O_6''.

n = Y in presence of added S_4O_6'' (concentration 0.1a.)

GRAPH TO SHOW THE ACCELERATING EFFECT OF SODIUM TETRATHIONATE.



a = b = 0·0425M.
pH = 7·40 μ = 1·84 Temp. = 35°C.

Time.	1 / 1 − x In presence of KCl.	In presence of $Na_2S_4O_6$.
0min. 0sec.	1·000	1·000
1 26	1·019	
1 33		1·035
2 54		1·058
4 39		1·071
5 24	1·042	
7 27		1·111
10 10		1·137
12 22	1·093	
13 6		1·180
15 10		1·186
16 15	1·118	
17 48		1·227
20 1		1·239
25 47	1·186	

FIGURE 23.

GRAPH TO SHOW THE VARIATION OF THE RATE OF REACTION WITH pH AT 25°C.

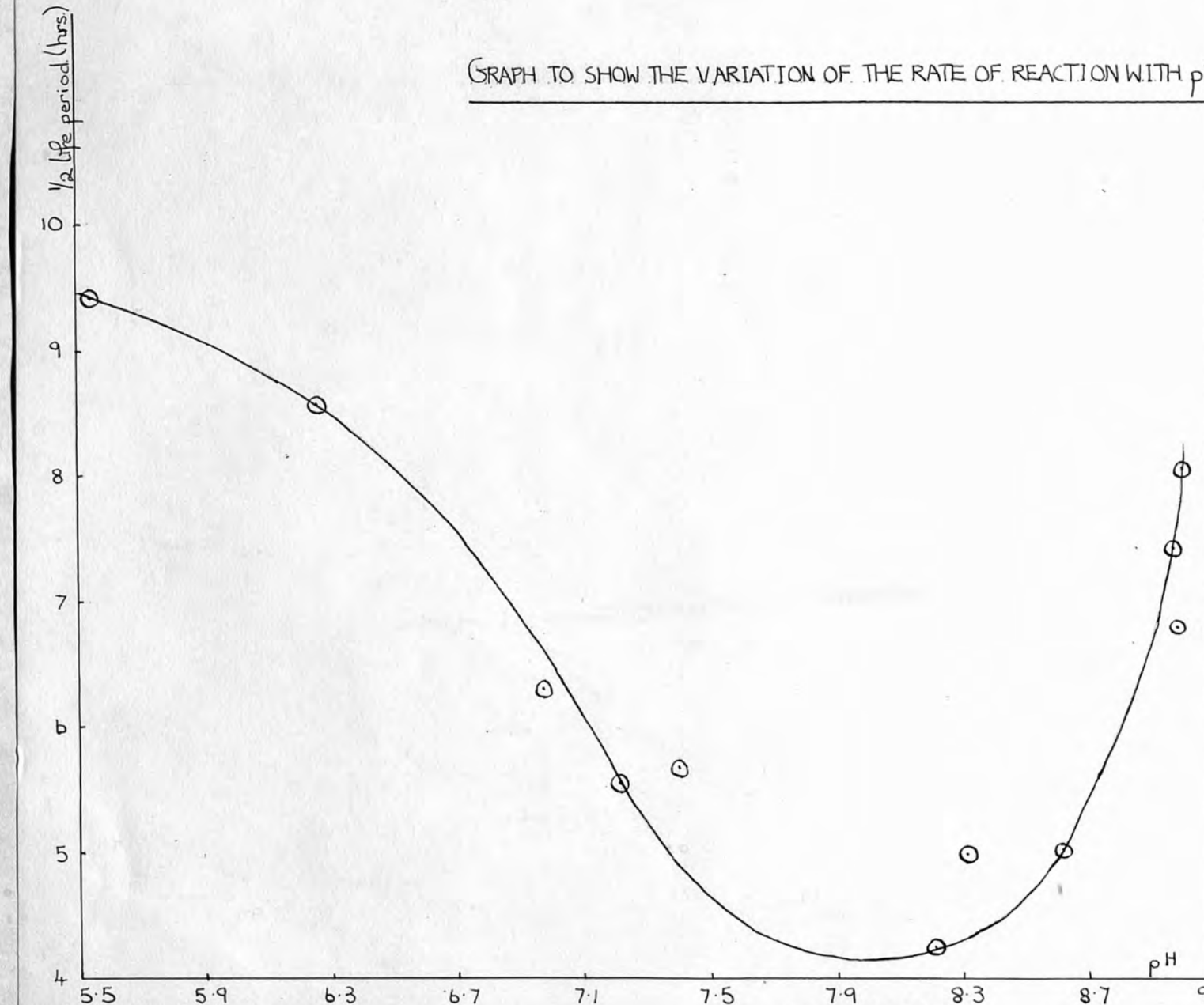


FIGURE 24.

pH	$k_1 \times 10^{-6}$	$k_2 \times 10^{-8}$	½ Life period.
5·53 25°	8·912		9hrs 20min
" 35°	19·30		5 18
6·25 25°	9·638		8 34
" 35°	21·20		3 24
6·97 25°		2·362	6 18
" 35°		4·593	3 11
7·21 25°		2·668	5 33
" 35°		4·982	2 54
7·40 25°		3·205	5 41
" 35°		5·359	2 48
8·21 25°		4·139	4 14
" 35°		6·903	2 22
8·31 25°		5·618	4 58
" 35°		10·07	2 30
8·62 25°		3·633	5 0
" 35°		6·123	2 47
8·97 25°		2·927	7 24
" 35°		5·487	3 16
8·98 25°		3·081	6 16
" 35°		4·671	3 41
9·00 25°		3·191	8 2
" 35°		4·827	5 30

(5) The retarding effect of ferrocyanide ions.

The general form of equation (8) indicates that a retardation through the addition of potassium ferrocyanide can arise in two ways:-

(a) By reduction of the term $\frac{Bk_3}{Ck_{-2}+Bk_3}$

(b) By increasing the term which has the form

$$\frac{2Cr_3}{\sqrt{AB}}\left(\sqrt{\frac{C^2r_3^2}{AB}+Y}-\frac{Cr_3}{\sqrt{AB}}\right)$$

If the initial concentrations of sodium thiosulphate and potassium ferricyanide are each a and the concentration of added potassium ferrocyanide is ac then the factor Y becomes

$$1-\frac{r_1x/2}{r_2(x+c)+1-x}$$

If the final retardation term is still regarded as negligible in the initial stages of the reaction (i.e. the retardation of type (b) above is neglected) and r_1 and r_2 are assigned the values 1628 and 4000, respectively, then the values of Y at various degrees of completion of the reaction, when the initial ferrocyanide concentration is one tenth and one half of that of the ferricyanide and thiosulphate, are as shown in Table $3^{(4)}$ of this chapter.

Table 3.(4)

Values of Y when $r_1 = 1628$ and $r_2 = 4000$

$ac = 0 \quad Y = 1 + \frac{814x}{3999x + 1}$ (Y_1)

$ac = 0.1a \quad Y = 1 + \frac{814x}{3999x + 401}$ (Y_2)

$ac = 0.5a \quad Y = 1 + \frac{814x}{3999x + 2001}$ (Y_3)

x	0.0	0.01	0.02	0.05	0.10	0.20	0.50	1.00
Y_1	1.00	1.199	1.200	1.202	1.203	1.2032	1.2034	1.2035
Y_2	1.00	1.018	1.034	1.068	1.102	1.135	1.170	1.185
Y_3	1.00	1.004	1.008	1.019	1.034	1.058	1.102	1.136

When other assumptions are made regarding the values of r_1 and r_2 the magnitude of these figures are altered slightly, but the relative values remain almost the same. They indicate that even a very small addition of potassium ferrocyanide reduces very considerably the contribution of the 'indirect mechanism' to the early stages of the reaction, but that the effect of this addition diminishes as the reaction proceeds. When the initial concentration of added ferrocyanide is half that of the ferricyanide and thiosulphate the repression of the indirect mechanism is such that when the reaction is 5% complete its contribution is less than one tenth, and when it

is 50% complete it is still less than half that in the absence of added ferrocyanide ions.

The net result, therefore, is that the addition of ferrocyanide ions leads to the very marked effect of tending to remove the initial abnormalities in the reaction rate, arising from the rapid increase in the rate of the indirect reaction in the early stages. The effect of this is that the $1 / (1-x)$ against t curves show an almost undetectable departure from linearity over the first half of the reaction.

As a result of measurements made at pH 6.1, Sandved and Holte found that the main effect of adding potassium ferrocyanide to the mixture of reactants was to remove the initial abnormalities, but they suggested no reason for this. It has been found in the present work, however, that at pH 7.40 the additions of ferrocyanide not only diminish the initial abnormalities but produce a general retarding effect. Although such is predicted by the mechanism suggested here, no similar general retardation was observed by Sandved and Holte.

The figures given in Table 3[4] (page 177) and similar calculations show that the relative rates of reaction with various initial concentrations of ferrocyanide, when the reaction is half complete should be as follows:-

$Fe(CN)_6''''$ added.	0.0	0.1a	0.2a	0.3a	0.4a	0.5a	a
Y	1.2034	1.170	1.145	1.127	1.113	1.102	1.051
% reduction.	0	2.8	4.9	6.4	7.5	8.4	12.7

This would suggest that the effect of ferrocyanide, arising from its suppression of the indirect reaction, will at this stage of the process increase progressively with the amount added, but that successive additions should produce progressively smaller effects. The results recorded in Tables 27[2] et seq., suggest, however, that the retarding effect, as compared with solutions of equal ionic strength without ferrocyanide addition, increases more nearly linearly with the ferrocyanide concentration than is indicated by these figures. The necessity of comparing solutions of equal ionic strength is, of course, a complicating factor which renders the precise interpretation of the results difficult. However, these results suggest the possibility of the final retardation term in the rate equation becoming significant at a relatively early stage of the reaction.

The form of the term

$$\frac{2Cr_3}{\sqrt{AB}}\left(\sqrt{\frac{C^2r_3^2}{AB}+Y}-\frac{Cr_3}{\sqrt{AB}}\right)$$

of equation (12) is of some considerable interest. When $Cr_3/\sqrt{AB}$ tends to become large with respect to $\sqrt{Y}$, the whole term tends to the value Y, which means that the reaction proceeds very slowly indeed, although not attaining a stable equilibrium state with finite concentrations of both reactants present. Thus when $Cr_3/\sqrt{AB} = 10\sqrt{Y}$ the term becomes 0.9974Y, whilst

even when $Cr_3/\sqrt{AB} = 2\sqrt{Y}$ it is still 0.944Y. On the other hand, as $Cr_3/\sqrt{AB}$ becomes small relative to $\sqrt{Y}$ the retardation term tends to the value $2Cr_3\sqrt{Y}/\sqrt{AB}$. Thus when $Cr_3/\sqrt{AB}$ is 0.5Y this term is $0.618\sqrt{Y} \times 2Cr_3/\sqrt{AB} = 0.618Y$ whilst when $Cr_3/\sqrt{AB}$ is 0.1Y it is $0.995\sqrt{Y} \times 2Cr_3/\sqrt{AB} = 0.199Y$.

It is evident that under the conditions pertaining when equimolecular mixtures of potassium ferricyanide and sodium thiosulphate are used in the reaction, the value of $Cr_3/\sqrt{AB}$ will increase rapidly as the end of the reaction is approached, and hence the kinetics will depart strongly from those to be expected from a second order process. Such a departure is actually observed when the extent of the reaction exceeds about 70%. Further, when the reaction is very near completion it seems to proceed very slowly indeed, so that there is always a very small amount of thiosulphate remaining after a period of several days, a factor which, at one stage of the investigation, was interpreted as indicating that an equilibrium state was reached whilst finite concentrations of the reactants were present.

A review of these circumstances makes it possible to assign a limit to the value of r_3. As retardation of a marked order begins only after the reaction is more than half complete, and the very slow part of the reaction begins only after it is 90% complete, the value of $2r_3$ cannot be greater than about 0.08. Further, since evidence has been obtained

that Y changes only from about 1.205 to 1.209 over this second half of the reaction no serious error is introduced into the argument by taking $\sqrt{Y}$ as 1.10 over the whole of the reaction for the purpose of discussing the order of magnitude of expected departures of the reaction rate from that predicted for a second order process.

Then $-\frac{dB}{dt} = k_1 ABY\left(1 - \frac{2xr_3}{(1-x)\sqrt{Y}}\right)$.

The values of the retardation term (R.T.) for varying values of x and r_3 are as follows (each value to be multiplied by $k_1 ABY$)

$2r_3$ x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0.08R.T.	0	0.008	0.019	0.031	0.047	0.073	0.110	0.170	0.291	0.655
	1	0.992	0.981	0.969	0.953	0.927	0.890	0.830	0.709	0.345
0.06R.T.	0	0.006	0.014	0.024	0.036	0.045	0.068	0.127	0.218	0.490
	1	0.994	0.986	0.976	0.964	0.955	0.932	0.873	0.792	0.510
0.04R.T.	0	0.004	0.009	0.016	0.024	0.036	0.054	0.084	0.145	0.327
	1	0.996	0.997	0.984	0.976	0.964	0.946	0.916	0.855	0.673

The observed departures from approximate second order kinetics could therefore be explained if the value of $2r_3$ lies within the limits 0.04 and 0.08, the best agreement with observation being obtained with a value of about 0.06. The figures given in the last table can be combined with the values of Y from Table 3 to give a combined factor by which ABk_1 must be multiplied to give the actual rate at various stages of the reaction. These are given in Table 4,(4) below, and indicate that over the first half of the reaction, at least, apart from the initial period of acceleration the effects of changes

in Y and in the retardation term tend to oppose one another, and lead to an almost imperceptible departure from second order kinetics.

Table 4.[4]

Rates at different stages of the reaction, assuming $r_1 = 1628$ $r_2 = 4000$ and $r_3 = 0.06$

$$\text{Rate} = ABk_1 \times Z$$

x	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Z	1.0	1.196	1.186	1.170	1.160	1.149	1.122	1.050	0.953	0.614

$$Z = Y\left(1 - \frac{2xr_3}{(1-x)\sqrt{Y}}\right)$$

On the basis of these assumptions it should also be possible to calculate the percentage retardation to be expected at any stage in the presence of added ferrocyanide ions, since the rate at any instant should be given by

$$-\frac{dB}{dt} = k_1ABY\left(1 - \frac{2(c+x)r_3}{(1-x)\sqrt{Y}}\right)$$

The results of such calculations are given in Table 5.[4]

These figures, although admittedly based upon somewhat arbitrary assumptions regarding the values of r_1, r_2 and r_3 indicate that the addition of ferrocyanide ions should diminish the initial abnormalities but that over the range 10 to 50% completion of the reaction it will still follow almost exactly a second order law. Comparison with the previous table indicates that the general retardation

produced through this part of the reaction should be of the order of 8-9%. This is less than is indicated by the results recorded in Table 30[2] but qualitatively the effect is of the type observed.

Table 5.[3]

Retardation produced by the addition of ferrocyanide ions.

c = 0.1a r_3 = 0.06

x	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
RT	0.006	0.013	0.022	0.034	0.050	0.072	0.105	0.160	0.270	0.600
1-RT	0.994	0.987	0.978	0.966	0.950	0.928	0.895	0.840	0.730	0.400
Y1-RT	0.994	1.088	1.110	1.107	1.100	1.086	1.050	0.989	0.863	0.474

R.T. = Retardation term.

The results are also of essentially the same type if other values are assigned to r_1, r_2 and r_3, so long as these bear the relationships to one another which are demanded by other observations. Further, this method of treatment indicates that the retardation will increase with increasing additions of ferrocyanide. (See Table 5a.[4])

Table 5a.[4]

Retardation produced by the addition of ferrocyanide ions.

c = 0.5a r_3 = 0.06

x	0.0	0.1	0.2	0.3	0.4	0.5	0.7	0.9
RT	0.030	0.040	0.052	0.069	0.090	0.120	0.240	0.840
1-RT	0.970	0.960	0.948	0.931	0.910	0.880	0.760	0.160
Y(1-RT)	0.970	0.993	1.003	1.000	0.990	0.972	0.776	0.182

The general retardation suggested here is of the order of 20% so the theory predicts that the retardation produced is less than proportional to the amount of ferrocyanide added.

Qualitatively, then, the results are explained by the theory but there is some possibility that there is an additional retardation term which has not been taken account of here, or that the ratio r_3 is greater than the value 0.06 used in these calculations. This could only be ascertained by further detailed study of the later stages of the reaction, a task which has proved difficult owing to the complication of the tendency for decomposition of the tetrathionate with liberation of sulphur when the mixture is allowed to stand for prolonged periods.

(6) The effect of hydrogen ion concentration.

As shown in Fig. 24, the reaction has a maximum velocity at about pH 8.0. At higher pH values the reaction is appreciably slower and, as indicated by the results recorded in Table 23 Chapter 2, at pH 11.2 it becomes very slow and has a pronounced induction period. This suggests that at high pH values the direct reaction becomes relatively unimportant as compared with the indirect reaction. The second dissociation constant of thiosulphuric acid is about 10^{-2}. Hence at pH 8 only about 10^{-6} of the thiosulphate ions are in the form $HS_2O_3^-$ which has been suggested earlier as a reacting species for the direct mechanism. At pH 11, however, this fraction is reduced to 10^{-9} and hence the direct reaction should be very much slower. The initial rate of reaction is therefore small, but as tetrathionate is formed by the slow direct reaction the indirect process gradually increases in importance; this leads to an increase in reaction rate as the tetrathionate concentration builds up but with a later retardation as the inhibitory effect of the ferrocyanide becomes increasingly pronounced.

Using the same nomenclature as earlier, the rate of reaction will again be given effectively by

$$-\frac{dB}{dt} = k_1 AB \frac{Er_1}{Cr_2 + B}$$

during the earlier stages of the process, or if the initial concentrations of the reactants are a and the proportion of the reactants decomposed is x, then

$$-\frac{dB}{dt} = \frac{k_1 a^2 (1-x)^2 x r_1}{2(xr_2+1+x)}$$

This will pass through a maximum when

$$\frac{d}{dx}\left\{\frac{(1-x)^2 x}{xr_2-x+1}\right\} = 0$$

$$\text{i.e. } \frac{1-4x+3x^2}{x(r_2-1)+1} - \frac{(r_2-1)(1-x)^2 x}{\{x(r_2-1)+1\}^2} = 0$$

Whence $x = 1$ or $r_2-1 = \frac{1-3x}{2x^2}$

A plot of the results given in Table 23[2] indicates that the maximum reaction rate occurs approximately when $x = 0.3$. Putting in this value

$$r_2-1 = \frac{1-0.9}{2x0.09} = \frac{0.1}{0.18} \quad \text{so } r_2 = 1.55$$

At first sight this result seems quite contradictory to the limits to the value of r_2 imposed by the measurements at pH 7.40 but it must be born in mind that $r_2 = k_{-2}/k_3$ and if the reverse process of reaction (2) really occurs between $HFe(CN)_6'''$ ions and S_4O_6' radicals, as in equation (10) k_{-2} should be replaced by $k_{-10}\left[H_3O^+\right]$ x2x10^4 so that $r_2 = k_{-10}\left[H_3O^+\right]$x 2 x 10^4 /$k_3$. Hence increase of pH from

7.40 to 11.2, corresponding to a decrease in r_2 by a factor of $10^{3.42}$ or 2,630. Accordingly, a value of 1.55 at pH 11.2 corresponds with a value of about 4000 at pH 7.40, a value which fits well with the results of the studies of the effects of tetrathionate additions at the lower pH value.

A further point which arises, however, is that if the indirect process involves S_4O_6'' ions whilst the direct process involves HS_2O_3' ions, the ratio r_1 should increase greatly with the increase in pH value and that, in fact, not being so strongly opposed by the reverse reaction the indirect process will proceed to yield products much more rapidly than at pH 7.40. It must be inferred, therefore, that the indirect process also involves ions of the type HS_4O_6' and that the ratio r_1 remains sensibly constant at about the value 1628. If this is the case, when the reaction is half complete the ratio of the rates of reaction, with equal initial concentrations and ionic strengths, at pH 11.2 and pH 7.40 would be expected to be

$$\frac{-\left(\frac{dB}{dt}\right)_{11.2}}{-\left(\frac{dB}{dt}\right)_{7.40}} \quad \frac{1}{2630} \times \frac{1 + 0.25\text{x}1628/1.27}{1 + 0.25\text{x}1628/2000.5} = 0.102$$

Comparison of the results recorded in Table 10[2] with those of Table 23[2] shows that when the reaction is 50% complete the actual ratio of the rates of reaction is approximately 0.6 : 1.

Similarly the ratio of the rates of reaction at pH 9.0 and pH 7.40 should be given by

$$\frac{-\left(\frac{dB}{dt}\right)_{9.0}}{-\left(\frac{dB}{dt}\right)_{7.40}} = \frac{1}{166}\,\frac{1 \times 1 + 0.25 \times 1628/120.5}{1 + 0.25 \times 1628/2000.5} = 0.22$$

Comparison of the results given in Tables 10[2] and 22[2] suggests that the ratio is actually about 0.3.

Although the discrepancies between these calculated and observed relative rates seem large, it is satisfactory that they are at least of the right order of magnitude, especially in view of the assumptions that have to be made. The direction of the divergencies observed is such that the rates at pH 9.0 and pH 7.40 are less than would be expected from the rate at pH 11.2. This divergence from the relative rates predicted by the mechanism so far suggested becomes even more acute at still lower pH values. The mechanism suggested would be expected to lead to higher rates of reaction, since, although the term arising from the indirect mechanism would be diminished, k_1 would be expected to increase with increasing hydrogen ion concentration. However, in fact, the rate of reaction diminishes as the pH value is lowered to 6, but at pH 5.5 it seems to have quite different kinetics, following a first order law more closely than a second order one.

The final retardation term will increase in relative

importance with increasing hydrogen ion concentration, and in this connection it may be significant that Sandved and Holte working at pH 6.1 found that retardation set in at an earlier stage than has been observed in this work at higher pH. Since Y is reduced almost to unity throughout the reaction the general rate equation (8) assumes the form

$$\frac{-dB}{dt} = k_1 AB\left\{1 - \frac{2Cr_3}{\sqrt{AB}}\left(\sqrt{\frac{C^2 r_3^2}{AB}+1} - \frac{Cr_3}{\sqrt{AB}}\right)\right\}$$

If the reactant mixture contains equal molar concentrations of sodium thiosulphate and potassium ferricyanide this becomes

$$\frac{-dB}{dt} = k_1 p^2 (1-x)^2\left\{1 - \frac{2r_3 x}{1-x}\left(\sqrt{\frac{r_3^2 x^2}{(1-x)^2}+1} - \frac{r_3 x}{1-x}\right)\right\}$$

As r_3 is predicted to be proportional to the square root of the hydrogen ion concentration a change in pH value of two units would be expected to increase the relative importance of the last term tenfold. At the same time this term should not influence the initial rate of the reaction but should rather cause the rate to fall off more rapidly than expected from a second order law as the reactants are consumed. This is just the reverse of observation at pH 5 where first order kinetics are approached.

The measurements at low pH values have been relatively few in number and the effects of additions of ferrocyanide and tetrathionate have not been studied under these conditions.

It is evident, however, that factors not considered when discussing the reaction at higher pH values must come into play. The fact that over the pH range 7.78 to 6 the rate of reaction tends to decrease instead of increasing as suggested by the proposed mechanism could be explained if the concentration of one of the reactants were effectively decreased by increased hydrogen ion concentration. It is difficult to see how this can occur, however, since Nekrassov and Zotov[25] found that even the third dissociation constant of ferricyanic acid is '' as high as that of hydrochloric acid '', whilst even at pH 5, only a small proportion of the thiosulphate will be in the form of $HS_2O_3^{'}$ ions and hence its passage into an unreactive form such as $H_2S_2O_3$ seems quite impossible.

It was not found possible to investigate the reaction in solutions buffered to pH values of less than 5.5 units, so little can be said in explanation of the tendency towards a first order reaction observed in the more acid solutions studied. It was noticed, however, in a trial run at pH 3.2 (Chapter 2. Section 1.) that colloidal sulphur was formed in the solution. It is possible, therefore, that the first order reaction may be accounted for by some form of surface reaction on this substance, some species of ions of either sodium thiosulphate or potassium ferricyanide being adsorbed. Alternatively it may be associated with a slow reaction of the type $HS_2O_3^{'} \longrightarrow HSO_3^{'} + S$, followed by a rapid oxidation

of the bisulphate ions by the ferricyanide.

Study of the reaction in unbuffered solutions showed that there were three distinct phases (Chapter 1. Section 2.) ---- an initial period of acceleration, followed by one of retardation and then a further slight acceleration. However, when the reaction was followed in buffered solutions the rate followed a more normal exponential type of curve.

These findings seem to be explained by the change of pH observed during the course of a run. (Chapter 3. Section 2.) As the pH of the solution decreases from its "original" value to 5.4 units the initial period of acceleration is observed. (It is impossible to read the original value of the pH since it is altering too rapidly for the instrument to give a steady reading.) The pH of the mixture then rises from 5.4 to 6.1 as the reaction rate decreases. It remains at this value and the rate decreases steadily with concentration.

CONCLUSIONS.

The observed rates of reaction between potassium ferricyanide and sodium thiosulphate in solutions buffered to pH 7.40 to 11.2 can be explained qualitatively but not completely quantitatively by a mechanism of the type

$$HS_2O_3^{'} + Fe(CN)_6^{'''} \rightleftharpoons S_2O_3^{'} + HFe(CN)_6^{'''}$$

$$HS_4O_6^{'} + Fe(CN)_6^{'''} \rightleftharpoons S_4O_6^{'} + HFe(CN)_6^{'''}$$

$$S_4O_6^{'} + S_2O_3^{''} \longrightarrow S_4O_6^{''} + S_2O_3^{'}$$

$$2\ S_2O_3^{'} \longrightarrow S_4O_6^{''}$$

The accelerating and retarding effects of added tetrathionate and ferrocyanide ion respectively are explained by this mechanism and permit the assignment of tentative values to the ratios of the rate constants of some of the reactions involved.

At very low pH values, however, the rates of reaction are much less than those predicted by this theory and the reaction tends to approximate to first order kinetics. This suggests that with increasing hydrogen ion concentration one of the reactant species passes over into a form which does not enter into the reaction or which participates only in an alternative and slower process. The available data regarding the dissociation constants of the relevant acids, however,

fails to throw any light on this aspect of the problem. The elucidation of the mechanism of the reaction at these lower pH values will demand further investigations, including studies of the effects of additions of tetrathionate and ferrocyanide ions.

The investigation can therefore only be regarded in the nature of a preliminary survey, but it has established a number of facts which had not been detected previously and has permitted tentative explanations to be put forward for many of them. For a more complete analysis of the problem more intensive studies are required upon such matters as

(a) the details of the early stages of the reaction, which could well be studied at very low concentrations,

(b) the details of the last stages of the reaction (beyond 80% completion) which has so far proved difficult owing to, inter alia the slight tendency for liberation of sulphur,

(c) the effect of ionic strength on the reaction at both the higher and lower limits of the pH range over which the reaction can be investigated,

(d) a reinvestigation of the dissociation constants of ferricyanic, ferrocyanic, thiosulphuric and tetrathionic acids.

Although, as yet, throwing only an indirect light upon the possible factors which complicate reactions such as that between ferricyanide and iodide ions, the present investigation indicates that before any definite mechanism can be assigned

to that process it will be necessary to study much more closely than has been done in the past the effects of factors such as ferrocyanide ions, on the reaction rate, as well as its dependence on pH.

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Appendix 1.

Standardisation of potassium ferricyanide solution.

25mls. of the potassium ferricyanide solution were mixed with 20mls. of approximately 10% potassium iodide solution. 2mls. of dilute sulphuric acid were then added followed by 15mls. of an aqueous solution containing 2g. of zinc sulphate. The liberated iodine was then titrated with standard sodium thiosulphate solution using starch indicator.

Appendix 2.

Preparation of sodium tetrathionate.[22]

A paste was made of 25g. of sodium thiosulphate ($Na_2S_2O_3,5H_2O$) 13g. of iodine and 5c.c. of distilled water. This was then rinsed into a small conical flask with 20c.c. of absolute alcohol. After standing for three hours it was filtered and washed free from iodine with alcohol. The residue was dissolved in 10c.c. of water at 35°C. and reprecipitated with 25c.c. of alcohol. Finally the purified sodium tetrathionate was left to dry over concentrated sulphuric acid in a vacuum dessicator.